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Electronic Supplementary Information (ESI)

High Yield Synthesis of Branched Gold Nanoparticles as Excellent Catalysts for the Reduction of Nitroarenes

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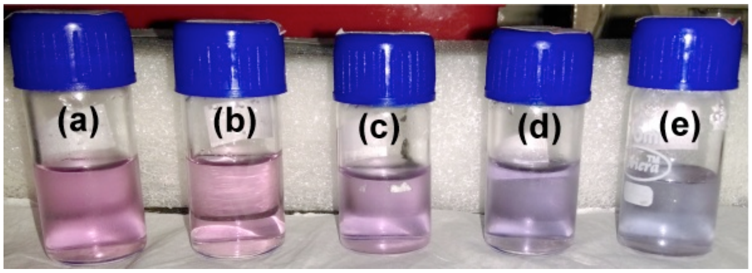


Figure S1. Photographic image of color of gold NPs using different concentration of acetanilide (a) 3.7 mM, (b) 7.4 mM, (c) 14.8mM, (d) 22.2 mM and (e) 29.5 mM.

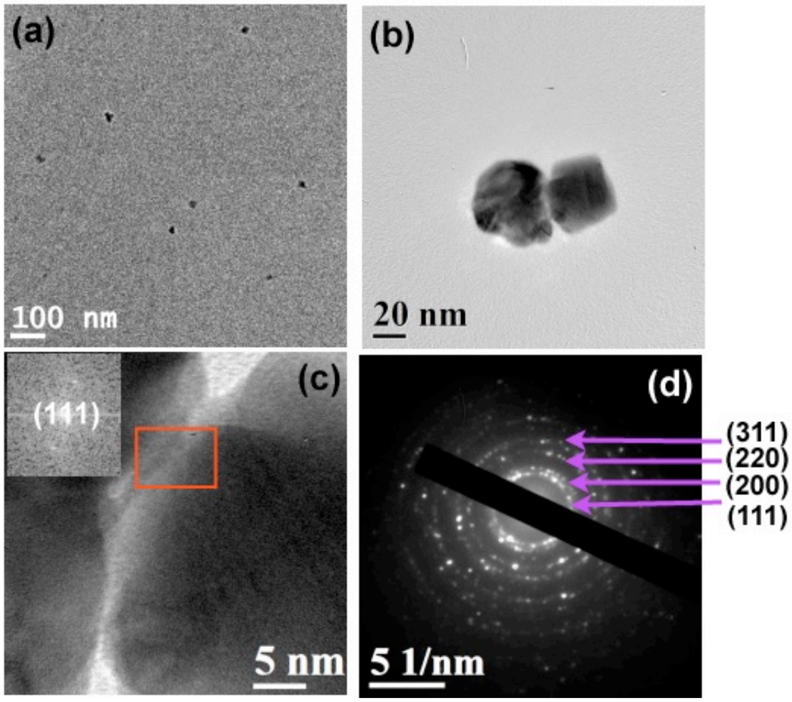


Figure S2. TEM and HRTEM image of gold NPs formation using 7.4 mM acetanilide. In set figure (c) shows the FFT image of the corresponding particles and (d) SAED pattern of gold NPs.

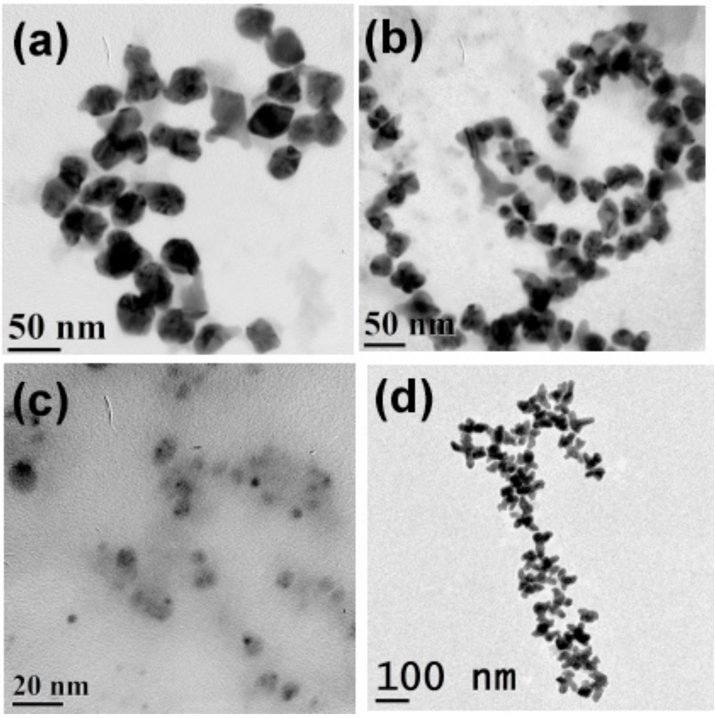


Figure S3. TEM image of gold nanostructure obtained using various concentration of acetanilide (a) 14.8 mM, 22.2 mM (b and c) and (d) 29.5 mM.

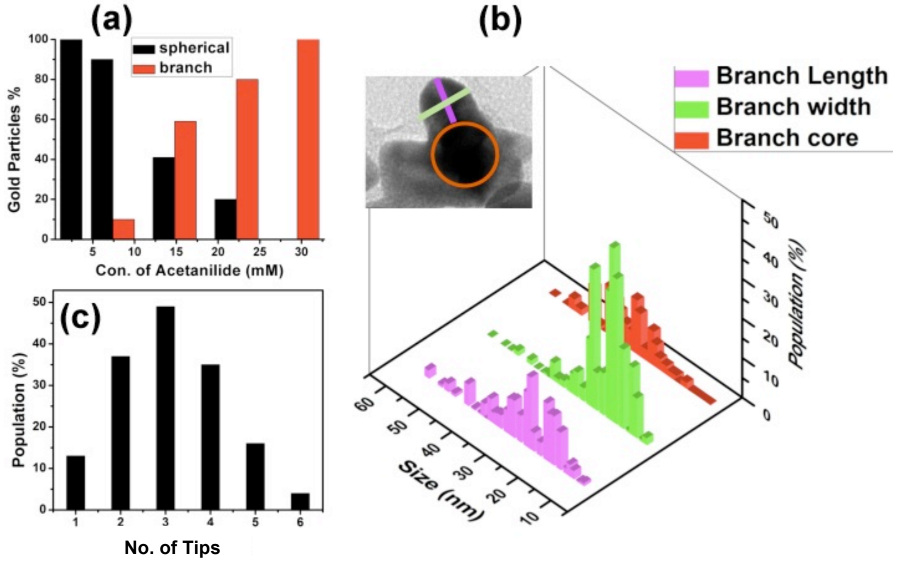


Figure S4. Population of spherical and branched gold NPs as a function of acetanilide concentration (a), (b) three dimensional plot of population of branch length, width and core of the branched gold NPs obtained at 29.5 mM of acetanilide. (c) Yield of branched gold NPs as a function of number of tips.

The percentage of spherical and branched gold NPs using different concentration of acetanilide was calculated. As shown in Figure S4a, both spherical and branched particles were calculated by analyzing more than 200 hundred particles from several TEM images. At lower concentration of acetanilide, the gold NPs have zero tips or no bud-like features were counted as spherical particles. The NPs containing bud-like feature and well-resolved tips around the spherical core was observed at higher concentration of acetanilide was counted as branched gold NPs. In order to calculate the number of tips around the spherical core of the branched gold NPs at 29.5 mM of acetanilide, more than two hundreds particles were collected from the several TEM images and analyzed. Zero tips indicated the spherical particles and one, two, three, four and five tips correspond to the increasingly complex branched gold NPs. As shown in figure S4c, 50-60% of the branched particles contain more than three tips and we have not observed any particles that contain zero tips. Since, TEM images were collected in two dimensional projection of three dimensional structure, all the tips around the spherical core of the branched particles may not be visible well and hence the analysis for the calculation of number of tips may not be so accurate.

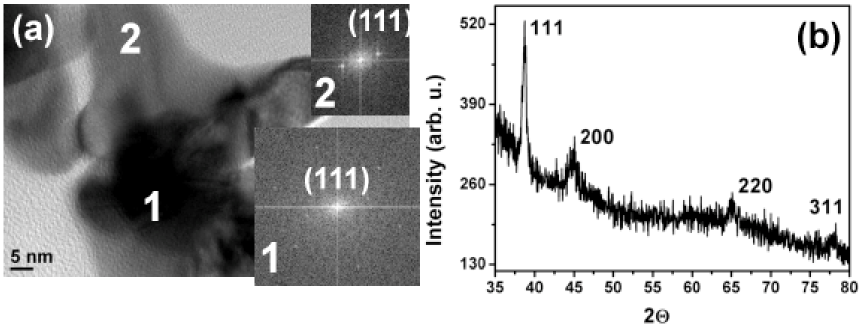


Figure S5. (a) High resolution TEM image single branched gold NPs obtained in the presence of 29.5 mM acetanilide. Right panel of this image shows the Fast Fourier Transform (FFT) pattern of this image (1) at the core and wings (2), respectively. (b) X-ray diffraction pattern of branched gold NPs.

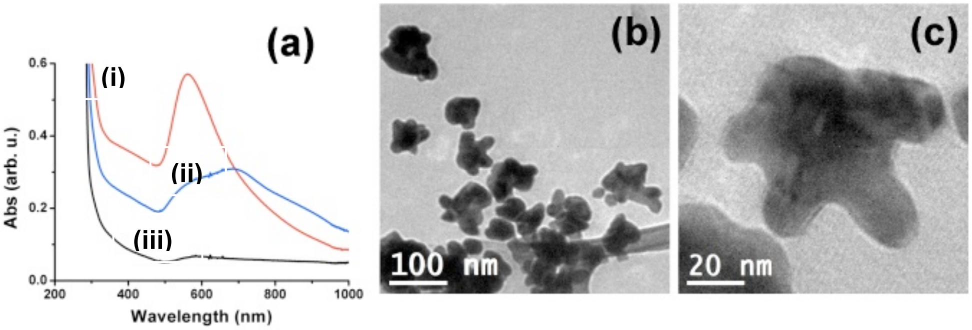


Figure S6. (a) UV-Visible spectra of gold NPs formation at 7.4 mM of acetanilide, (ii) addition of 22.2 mM of acetanilide into (i) and (iii) excess amount of $HAuCl_4$ (80 µM) was added into (i). (b) TEM image of branched gold NPs obtained from solution of (ii) and (c) is expanded view of (b)

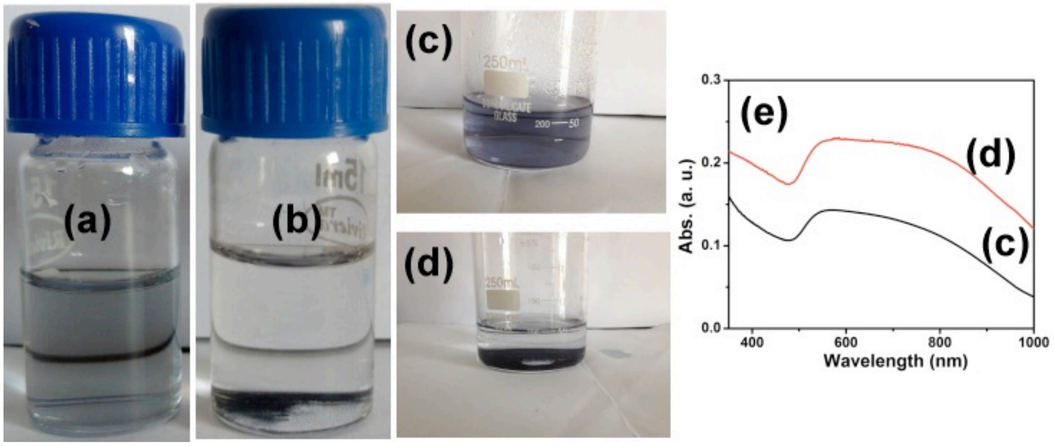


Figure S7. Photographic image of branched gold NPs solution obtained using 29.5 mM acetanilide (a) and (c). (b) and (d) branched gold NPs precipitate formation after seven days. (e) UV-Visible spectra of branched gold NPs.

<u>Determination of gold content in the isolated branched gold NPs</u>

Table S1. Concentration of Au content in the isolated branched gold NPs catalysts determined by ICP-OES.

In vial (10 mL reaction mixture)	***Gold content (μM)***
Before reduction	40
After reduction in one vial (in the branched gold NPs)	39.2

The bulk precipitate was collected from twenty vials (only from higher amount of acetanilide (29.5 mM) contained vials), which is recovered and purified by decantation of the liquid using micropipette and followed by washing with Milli-Q grade water for 5 times. The recovered and isolated precipitate was redispersed in 100 mL water and stored in a refrigerator for catalytic studies. The final concentration of gold content in the isolated branched gold NPs was determined to be 78.4 μM. The ratio of gold and acetanilide was determined as 1:6 from the dried powder of branched gold NPs.

Estimation of acetanilide in the isolated branched gold NPs

The bulk precipitate was collected from the five vials, which was isolated and dried at 40 ^{o}C under hot air oven for over night to obtain the pure powder. Thermo Gravimetric Analysis (TGA) was carried out for dried powder and the corresponding spectra are shown in Figure S8. This spectrum were recorded using a simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter in nitrogen atmosphere for temperature range 20°C to 800°C at a heating rate of 10°C/min. This spectrum shows a single sharp weight loss in TGA starting at 221 °C. This monotonic weight loss was attributed to complete decomposition of the acetanilide molecules bounded to the branched gold NPs surface. The content of acetanilide in the branched gold NPs was determined from TGA and found that five acetanilide molecules are required to stabilize one gold atom in the branched gold NPs (Table S2).

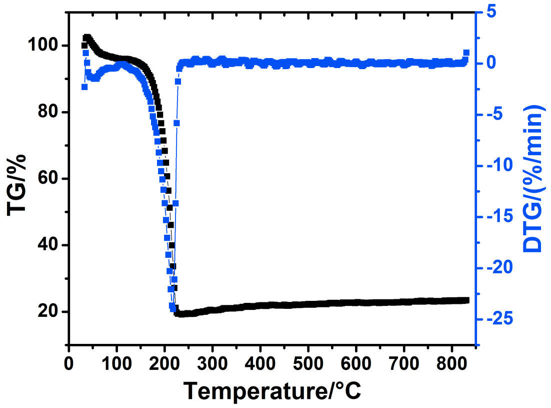


Figure S8. Thermogravimetric analysis profile of isolated branched gold NPs.

Table S2. The content of acetanilide in the branched gold NPs was determined using TGA analysis.

Process	Amount of acetanilide (g)	Amount of gold (g)	Number of acetanilide molecules required to stabilize one gold atom
Before Isolation	0.2	0.00039	512
After Isolation	0.0021	0.00039	5.5

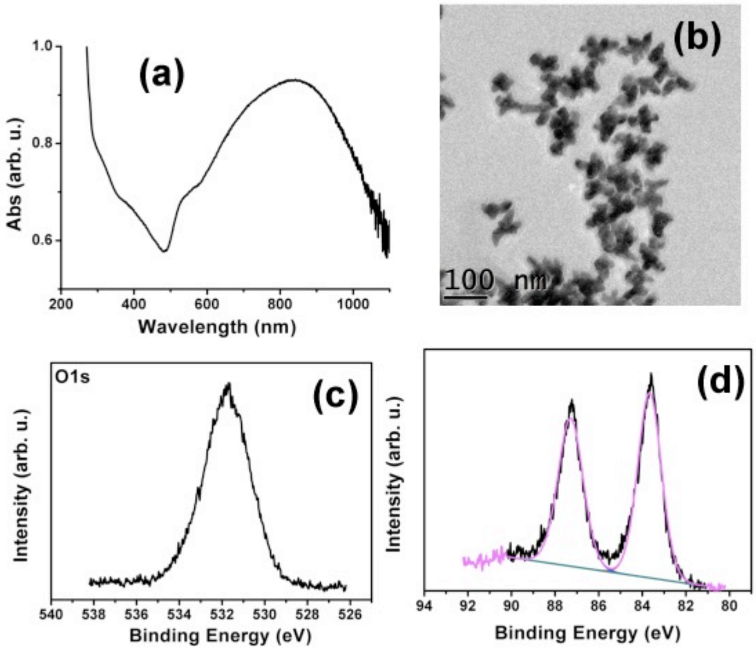


Figure S9. (a) and (b) UV-Visible spectrum and TEM image of isolated branched gold NPs. (c) and (d) XPS spectrum of O1s and Au 4f core peak of branched gold NPs.

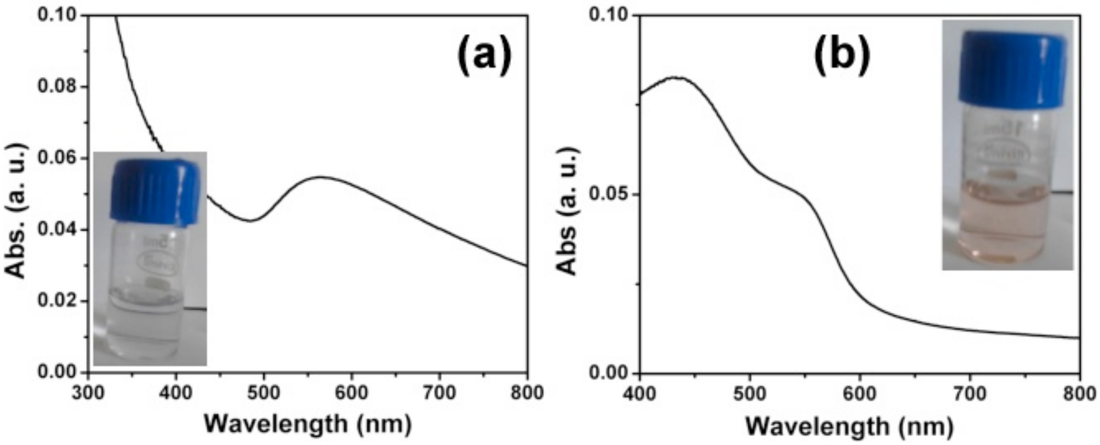


Figure S10. The UV-Visible spectra of branched gold NPs formation using (a) acetic acid and (b) aniline. Inset figure shows the photographic picture of color of gold NPs formation.

Figure S9a shows the absorption peak at 550 nm, which is characteristic SPR band of gold NPs. The formation of gold NPs due to the trace amount of impurities such as aldehyde, formic acid and other oxidisable species might contain in the acetic acid[1].

Calculation of the available surface area of the branched gold NPs

In order to prepare the standard calibration curve of the 4-nitrothiophenol (4-NTP), a known concentration of aqueous solution of 4-NTP was prepared by diluting the 0.1 mM stock solution at room temperature. Then, fixed amount of branched gold NPs (3.23 µg) was mixed with various amount of 0.1 mM stock solution of 4-NTP solutions. The mechanical stirrer at 500 rpm was used to shake this mixture for 5 hrs. The resulting solution was then centrifuged at 5000 rpm for 40 mints and the supernatant was collected in a separate vial to measure the unadsorbed amount of 4-NTP using the extinction coefficient of 4-NTP (Figure S11a). The equilibrium concentration was calculated from the absorbance peak intensity after adsorption. The moles of adsorbed 4-NTP per gram of branched gold NPs was calculated by dividing the total amount of adsorbed 4-NTP by weight of gold present in the branched gold NPs solution. The adsorption isotherm was then generated by dividing the number of moles of adsorbed 4-NTP per gram of branched gold NPs with the equilibrium concentration of 4-NTP (Figure S11b). The Langmuir isotherm is a relationship between the equilibrium concentrations of 4-NTP divided by adsorbed moles of 4-NTP per gram of branched gold NPs versus the equilibrium of concentration of 4-NTP (Figure 11c). The slope of the Langmuir plot will give the reciprocal of the number of moles of 4-NTP per gram of branched gold NPs, so the active surface area can be calculated using the following eq:

Surface area = 1/slope x (N_A) x 0.87×10^{-18} m^2

Where N_A is Avogadro's number and the value of 0.87×10^{-18} m^2 is area of 4-NTP.

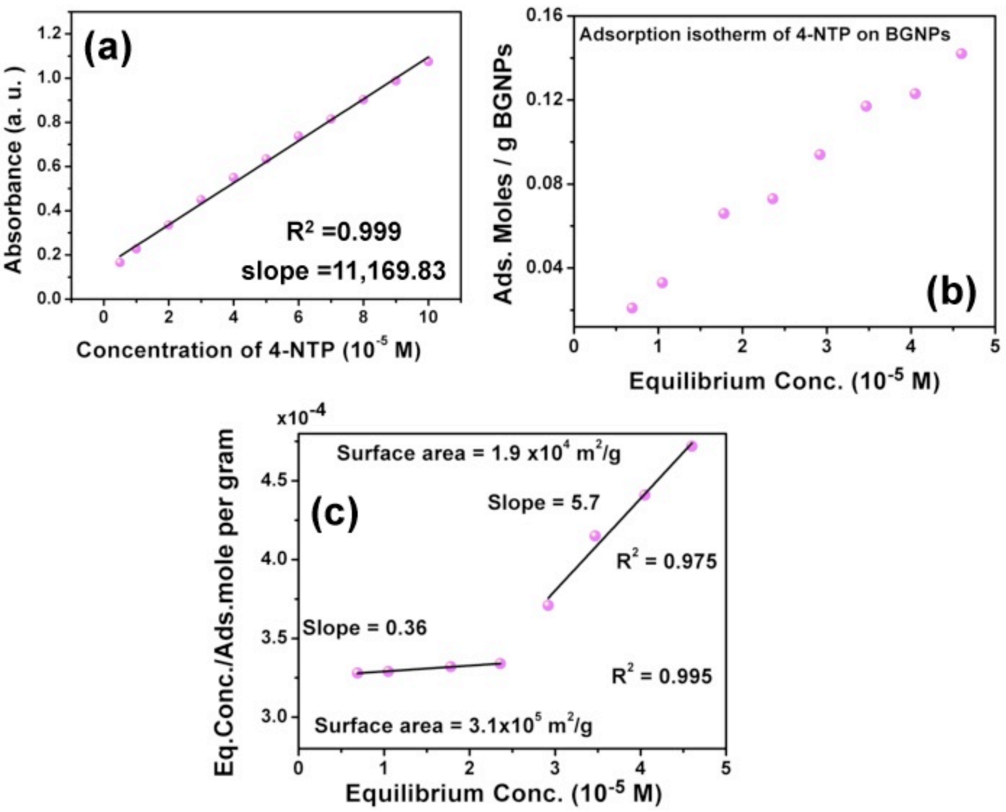
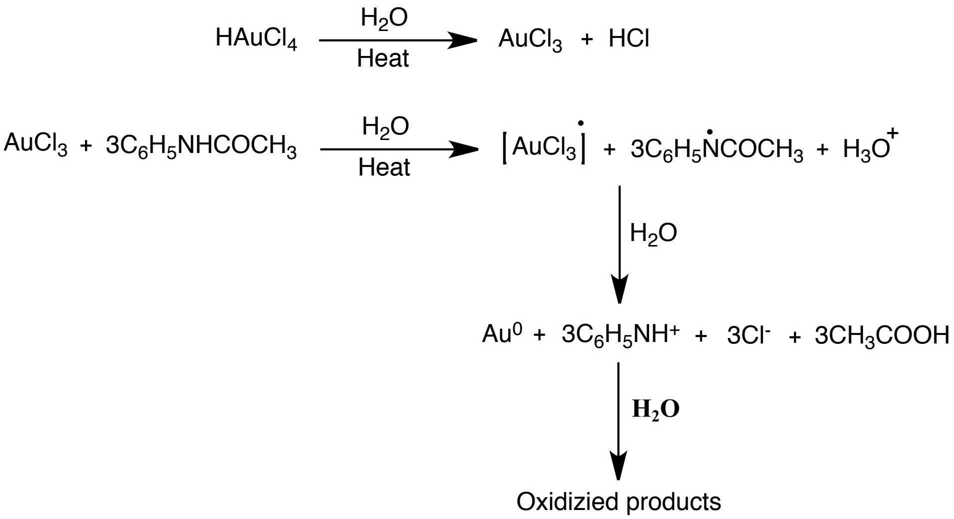


Figure S11. (a) Standard calibration curve of absorbance of 4-NTP at 420 nm with various concentration of 4-NTP. (b) Adsorption isotherm of 4-NTP on branched gold NPs and (c) Langmuir isotherm of the adsorption of 4-NTP on the branched gold NPs.

Reduction of $HAuCl_4$ by acetanilide

As evidenced from the control experiment that the products of aniline and acetic acid thus possibly formed from hydrolyze of acetanilide in aqueous acidic condition did not involve any role as capping or stabilizing agents for the formation of branched gold NPs. Therefore, the probable mechanism for the reduction of $HAuCl_4$ by acetanilide can be proposed as shown in scheme S1. Acetanilide may coordinate with $HAuCl_4$ complex through nitrogen and oxygen atom of the carbonyl group to give an electron deficient complex and followed by the reaction with water molecules leads to the formation of a free radical intermediate. These free radicals might undergo hydrolytic fission to give anilinium free radicals, which further reduce the gold ion into gold atom to produce the anilinium ion followed by reaction with water molecules to yield oxidized products that are washed away from the precipitates during the isolation process[2].



Scheme S1: Plausible mechanism of reduction of gold ion by acetanilide.

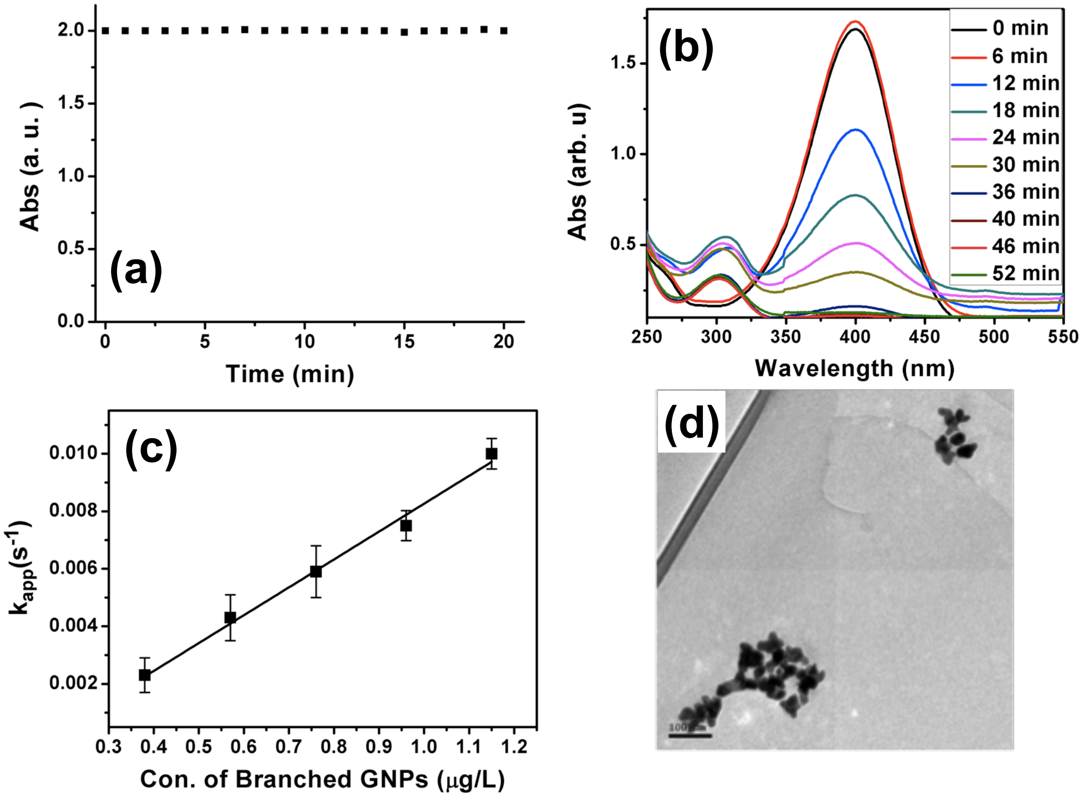


Figure S12. UV-Visible spectra of solution of 4-NP measured at different time intervals (a) in the absence of branched gold NPs catalysts and (b) in the presence of 0.39 μM of branched gold NPs catalysts and (c) Plot of apparent rate constant (k_{app}) as a function of amount of branched gold NPs catalysts. (d) TEM image of branched gold NPs catalysts after the reduction reaction is completed. This image is taken from the 2.37 μM branched gold NPs catalysts containing reaction mixture.

Preparation of acetanilide stabilized spherical gold NPs

2.2 mM of acetanilide was dissolved in 50 mL hot water, in which 600 μL of 20 mM $HAuCL_4$ (0.24 mM) was mixed and the resulting mixture was stirred for 5 min at room temperature. To this solution, 1.2 mL of 26 mM of freshly prepared $NaBH_4$ was added and the stirring was continued for one and half hour. The ratio of gold and acetanilide was maintained as 1:6.

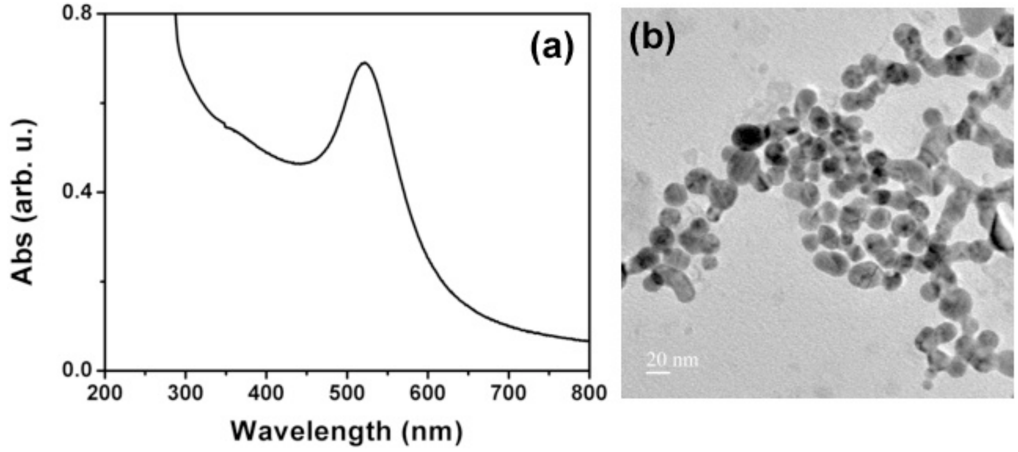


Figure S13. (a) UV-Visible spectra of spherical gold NPs and (b) TEM image of spherical Au NPs.

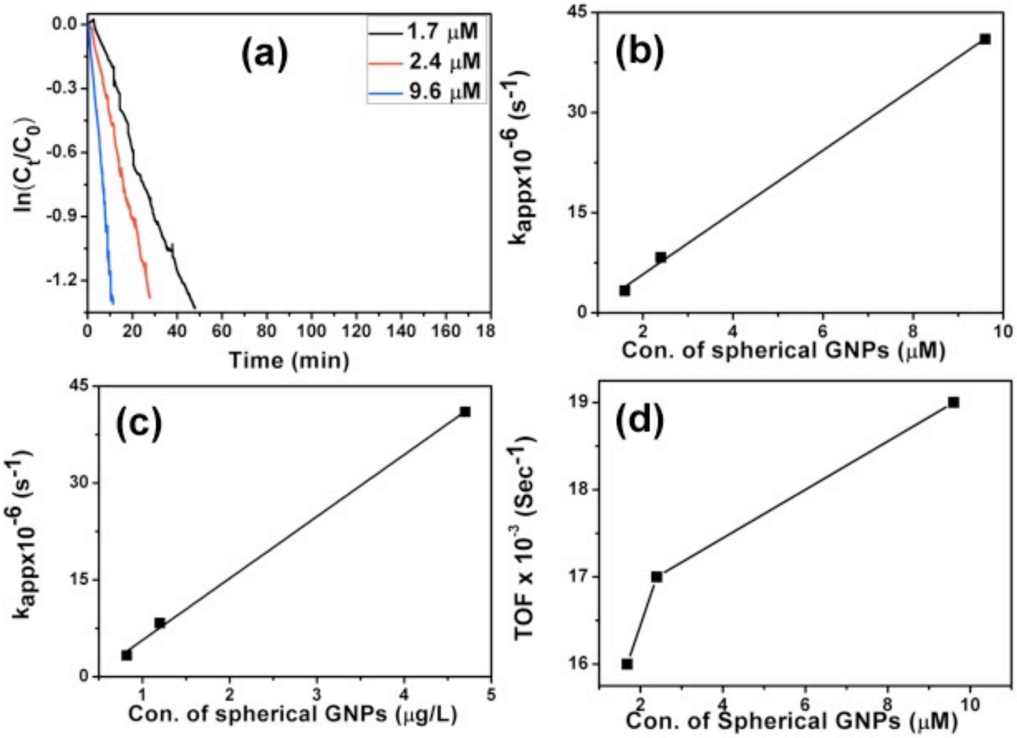


Figure S14. (a) The plot of $\ln(C_t/C_0)$ at λ_{max} of 4-NP versus different concentration of spherical gold NPs catalysts. (b and c) Plot of apparent rate constant (k_{app}) with function of spherical gold NPs concentrations. (d) Plot of TOF versus function of spherical gold NPs concentrations.

TOF calculation

Turn over frequency was defined as number of molecules reacted or product formed per active sites per unit time.

$$\mathrm{TOF} = \frac{\mathrm{M}}{\mathrm{N} \times \mathrm{t}}$$

Here, M stands for molar concentration of 4-NP and N is the molar concentration of gold in the branched NPs catalysts and t is the time taken to complete conversion of 4-NP into 4-AP. In contrast to isotropic metal NPs, branched gold NPs possess a complex structure required some theoretical modeling to determine the number of active surface atoms, which is out of scope of this present study. Furthermore, it has been reported in several articles that turn over frequency of metal NPs catalyzed surface reaction was mentioned as hour^{-1}, moles of reactant hour^{-1}. mole of catalyst^{-1} and $\text{g}^{-1}.\text{s}^{-1}$, etc[3].

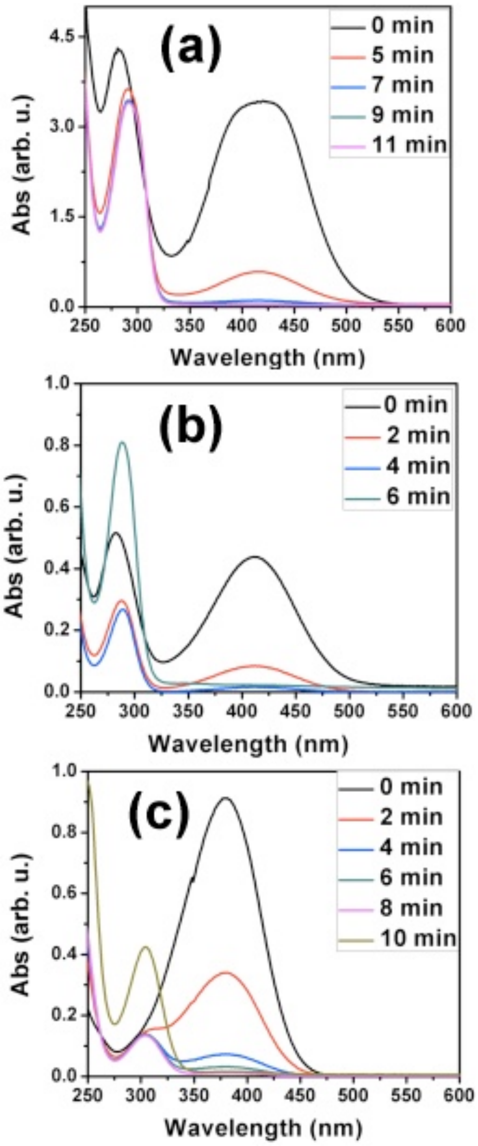


Figure S15. (a), (b) and (c) branched Au NPs catalyzed reduction of *o*-nitrophenol, *o*-nitroaniline and *p*-nitroaniline, respectively. Concentration of the branched gold NPs used in the reduction reaction is 1.95 µM.

References

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2. R. Gupta, *Monatshefte fur Chemie.,* 1990, **121**, 571 – 576.

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