

Supporting information

Green Synthesis of Gold Nanoparticles Using Aqueous *Aegle marmelos* Leaf Extract and its Application for Thiamine Detection

K. Jagajjani Rao and Santanu Paria*

Interfaces and Nanomaterials Laboratory, Department of Chemical Engineering, National Institute of Technology, Rourkela–769 008, Orissa, India.

*Corresponding author. E-mail address: santanuparia@yahoo.com, or paria@nitrrkl.ac.in;
Fax: +91 661 246 2999

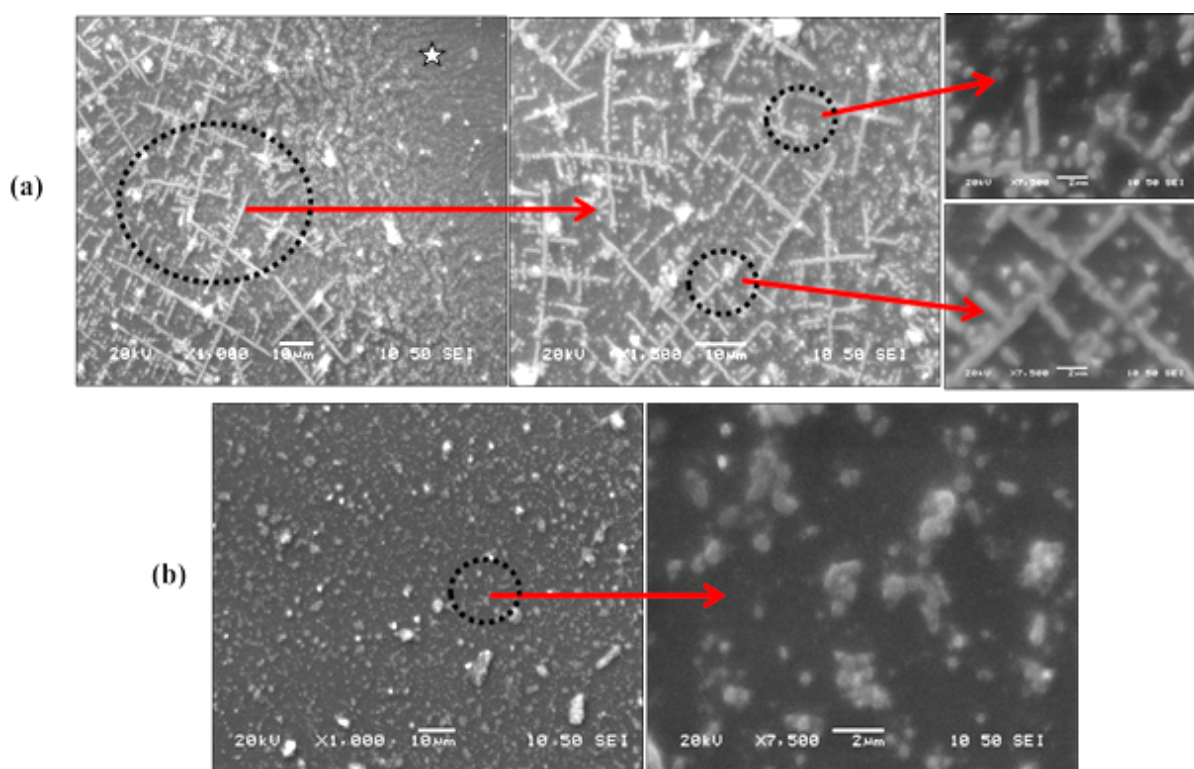


Figure S1. (a) SEM images of self-assembled structure of AuNPs formed from 1.0 mM/ 0.2 % (HAuCl₄/LE) on glass substrate. (b) Water washed AuNPs separated via centrifugation after synthesis. Suspension was dropped on glass surface and shows absence of self-assembled structure.

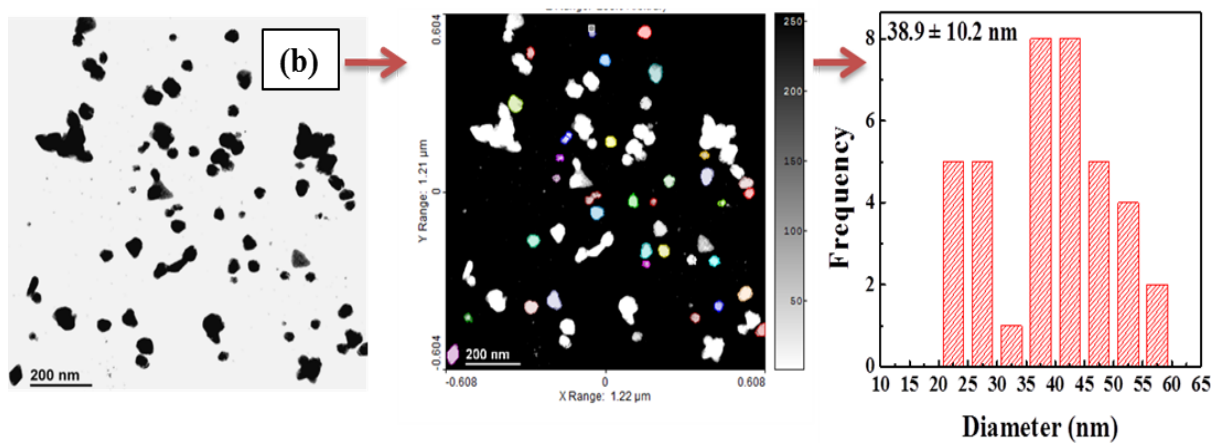
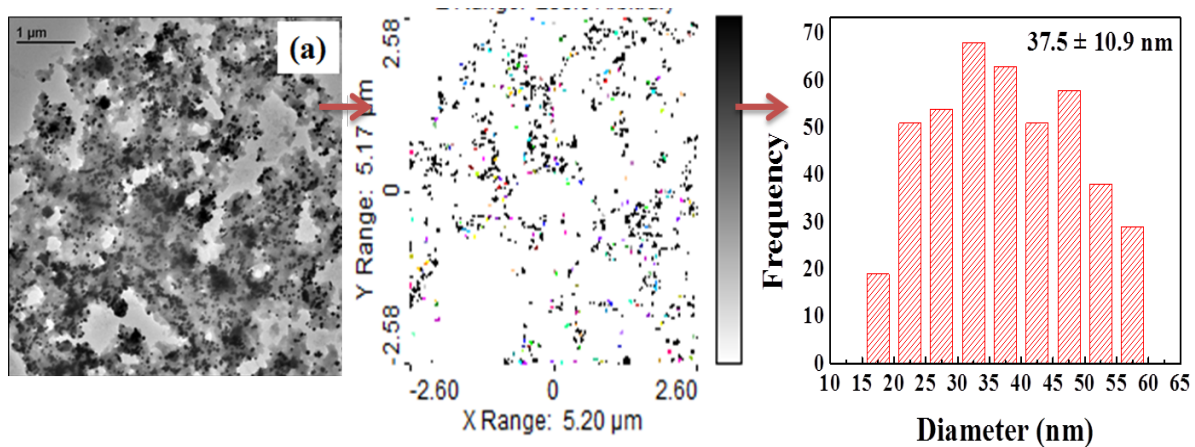


Figure S2. Particle size histograms of the TEM images of AuNPs formed from 1.0 mM/ 1.5 % (HAuCl₄/LE). (a), (b) are low and high magnification images.

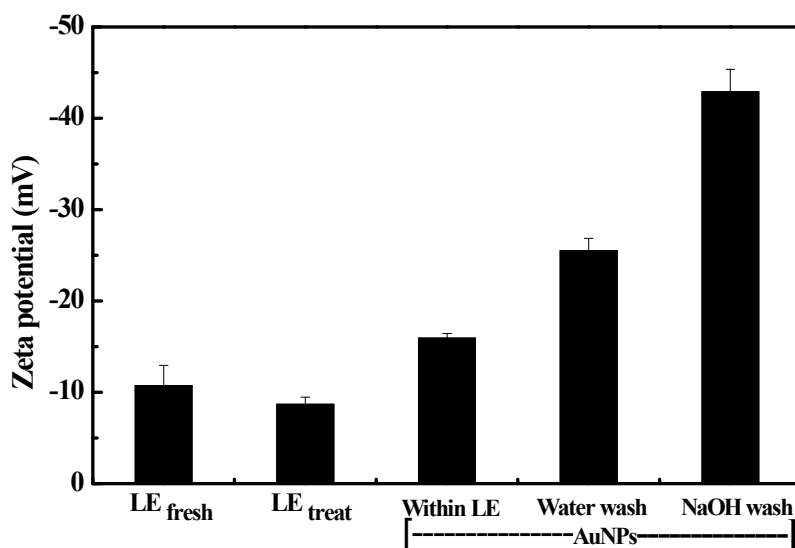


Figure S3. Zeta potentials of LE before and after reduction of Au salt, as-synthesized, water washed and NaOH treated AuNPs. Values observed are at pH ~7.0.

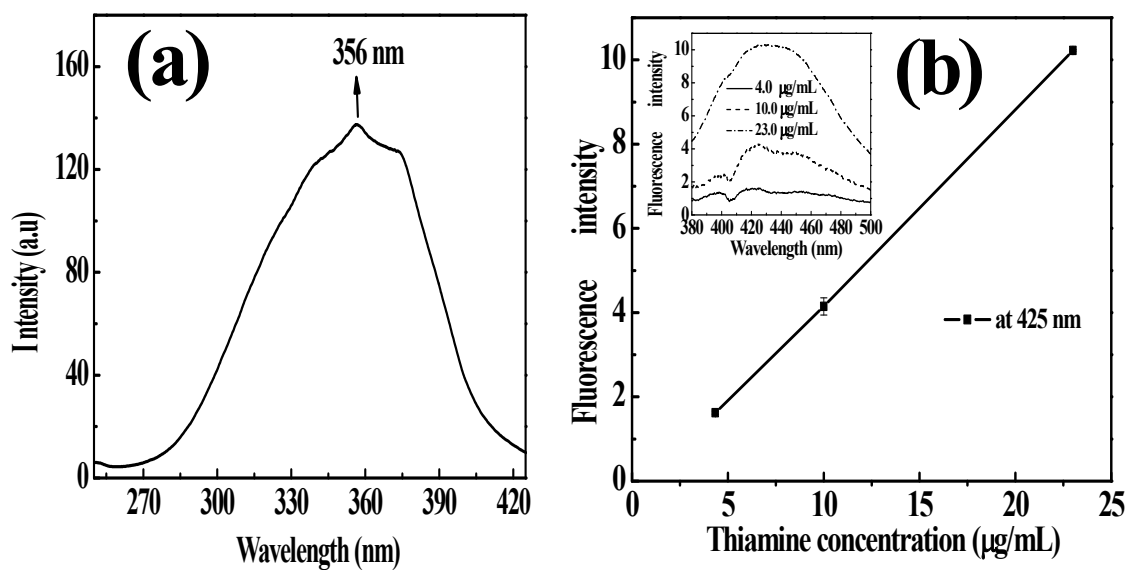


Figure S4. (a) Excitation maximum observed and used for the experimentation. (b) Fluorescence signal intensities of different concentrations of pure LE on exposure to 0.5 µM Thi. Spectral signals in full given in figure insert.

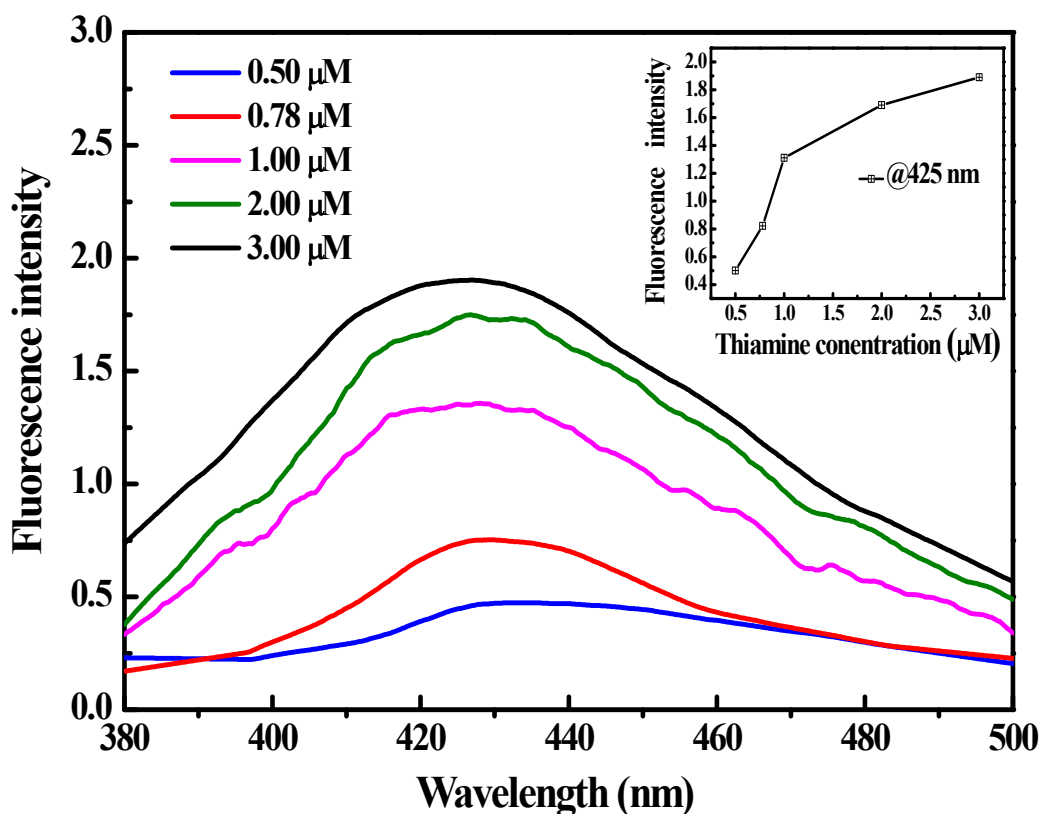


Figure S5. Spectra of thiamine (0.5 to 3.0 μM) exposed to 92.5 $\mu\text{g/mL}$ capped AuNPs obtained from NaBH_4 reduction and exposed to LE. Insert of (b) displays the fluorescence signal at fixed λ_{emi} of 425 nm with respect to increase in thiamine concentration.

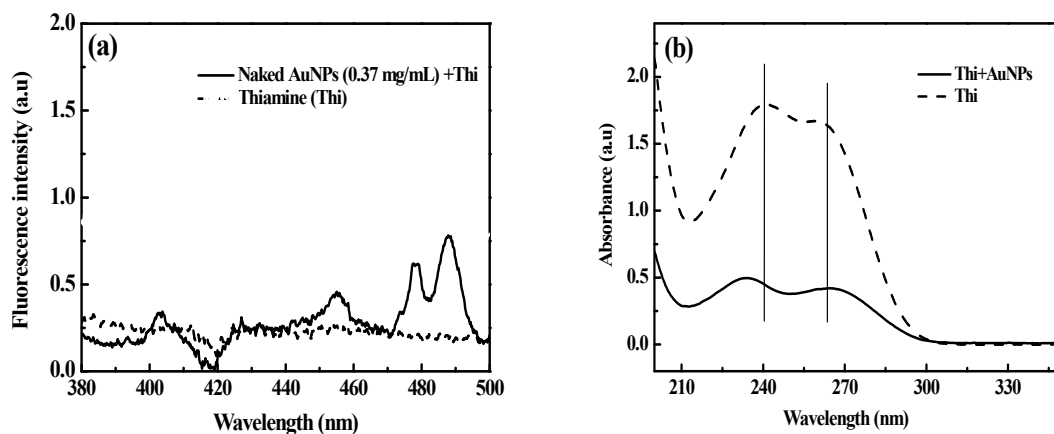


Figure S6. (a) Fluorescence signals of pure thiamine and naked AuNPs upon excitation at 356 nm. (b) UV-vis absorption spectra of thiamine (20 μM) in presence (Thi+AuNPs) and absence (Thi) of tannin capped AuNPs (2.32 mg/mL) at pH of 6.0.

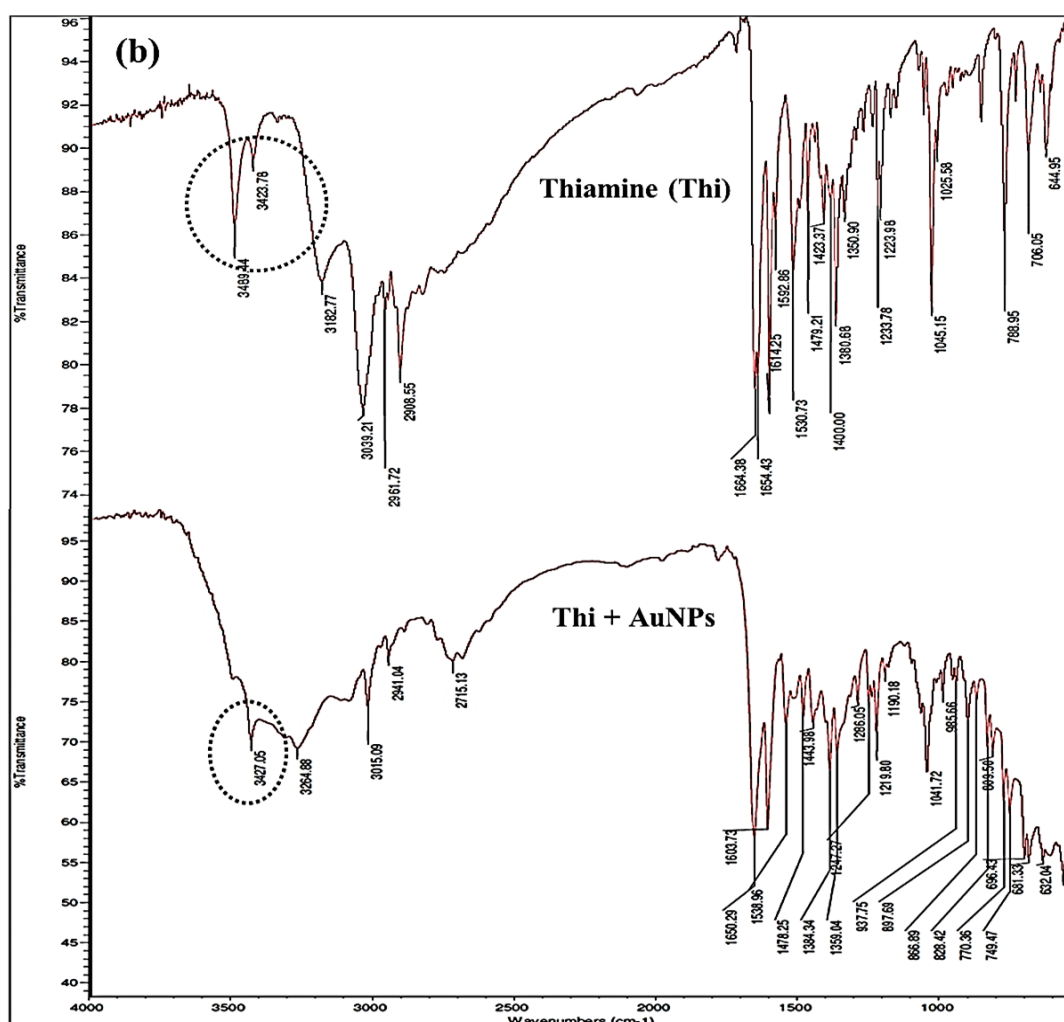
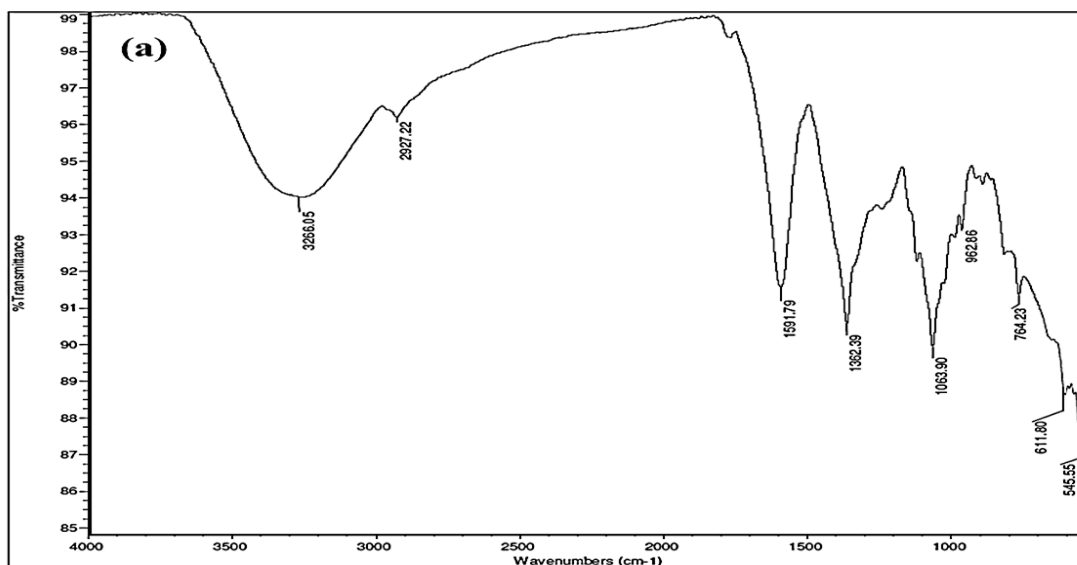


Figure S7. ATR-FTIR spectra of the capped AuNPs (a) and pure thiamine (Thi) before and after treatment with capped AuNPs (Thi+AuNPs). Major changes in the spectra are indicated in rounded dotted line.

IR analysis - oxidation of Thiamine

FTIR characterization was done to gain insights about the oxidation of thiamine to thiochrome by capped polyphenols at AuNPs surface. Figure S7a shows the complete spectrum of water washed AuNPs with significant absorption bands at 3266, 2927, 1591, 1362, 1063 cm^{-1} and peaks in the region of 400 – 1000 cm^{-1} . This band pattern of the functional group as well as the finger print region is similar to that of polyphenols (like tannin derivative) as specified in our previous study (Jagajjanani Rao & Paria 2013). From the figure, peaks at 3266 (OH stretch), 2927 (aromatic C-H stretch), 1591 (for C=C), 1362 (for OH group), 1064 (for C–O stretch) along with small peaks at 764, 611 and 545 of 800– 600 cm^{-1} region (for C–H out of plane bend) attributes to the characteristic of tannic acid product on the SNP's surface; which are responsible for the capping and particle stabilization.

Further upon the usage of these capped AuNPs for Thi oxidation; the variations before and after oxidation were observed by investigating their FTIR spectra. Figure S7b shows the IR spectrum of pure Thi before and after oxidation (Thi+AuNPs). The spectral pattern of Figure S7b (Thi) indicate the native thiamine hydrochloride spectrum (NIST 2011; SDBS n.d.) and the existence of aromatic primary amine (N-H stretch) absorptions at the region 3200 to 3500 cm^{-1} , with the presence of a particular fang type peaks at 3423 and 3489 cm^{-1} (Coates 2000).

The observed peak pattern when compared with Figure S7b (Thi+AuNPs) shows the major difference was observed only at 3200 to 3500 cm^{-1} band region, while all the other peaks remained almost same as Thi. The absence of fang type peaks and peak at 3427 cm^{-1} indicate the presence N-H stretch due to a secondary amine in the structure (Coates 2000). This change infers that the added Thi might be oxidised to thiochrome where secondary amine conjugates the pyrimidine and thiazole rings of Thi to form a fluorescent compound. The oxidation property of the capping agent of AuNPs towards Thi can be effectively utilized for its precise detection.

Coates, J. *Interpretation of Infrared Spectra, a Practical Approach*; Wiley Online Library, **2000**.

Jagajjanani Rao, K.; Paria, S. Green synthesis of silver nanoparticles from aqueous *Aegle marmelos* leaf extract. *Mater. Res. Bull.* **2013**, *48*, 628–634.