Green synthesis of Au, Pd and Au@Pd core-shell nanoparticles via tryptophan induced supramolecular interface.

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1. **HRTEM and STEM Images of Au@Pd NPs.**
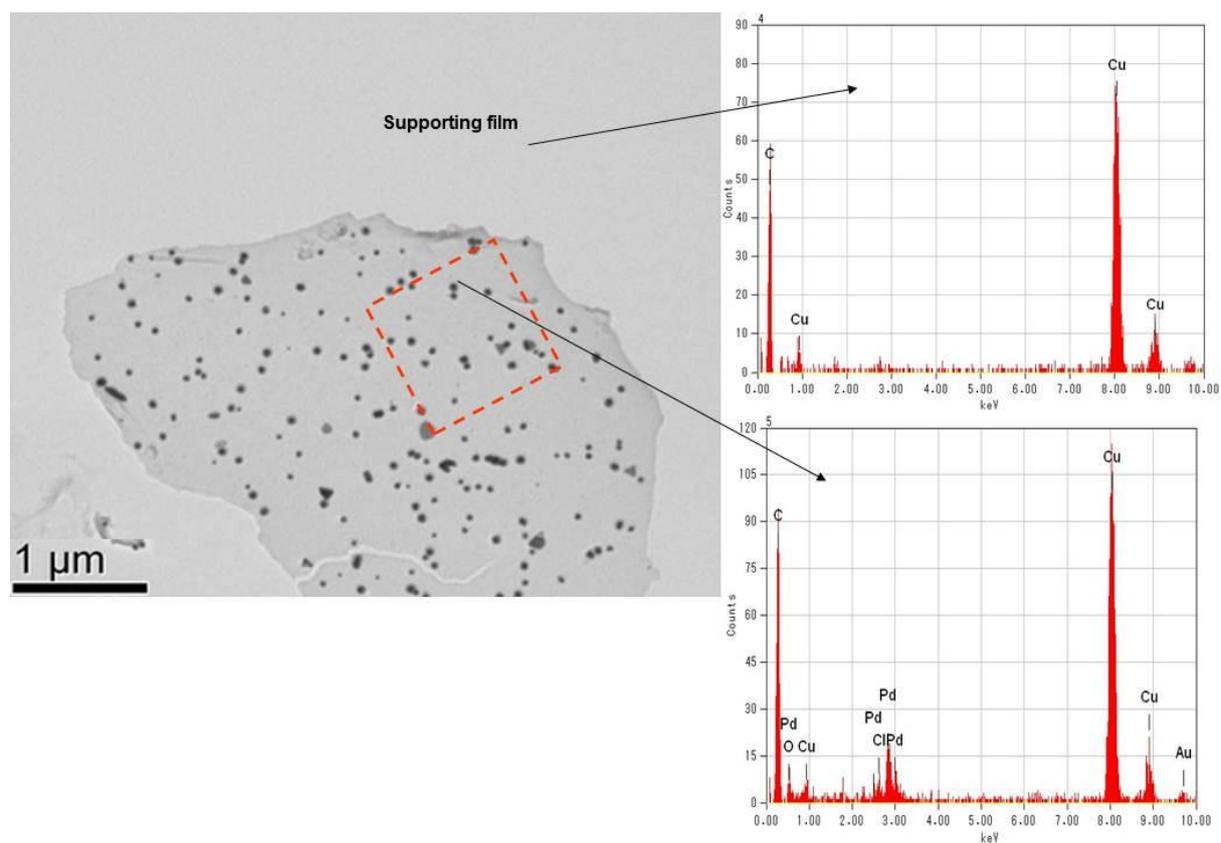
Figure S1 Showing the two distinct grid regions containing sample and without sample load.
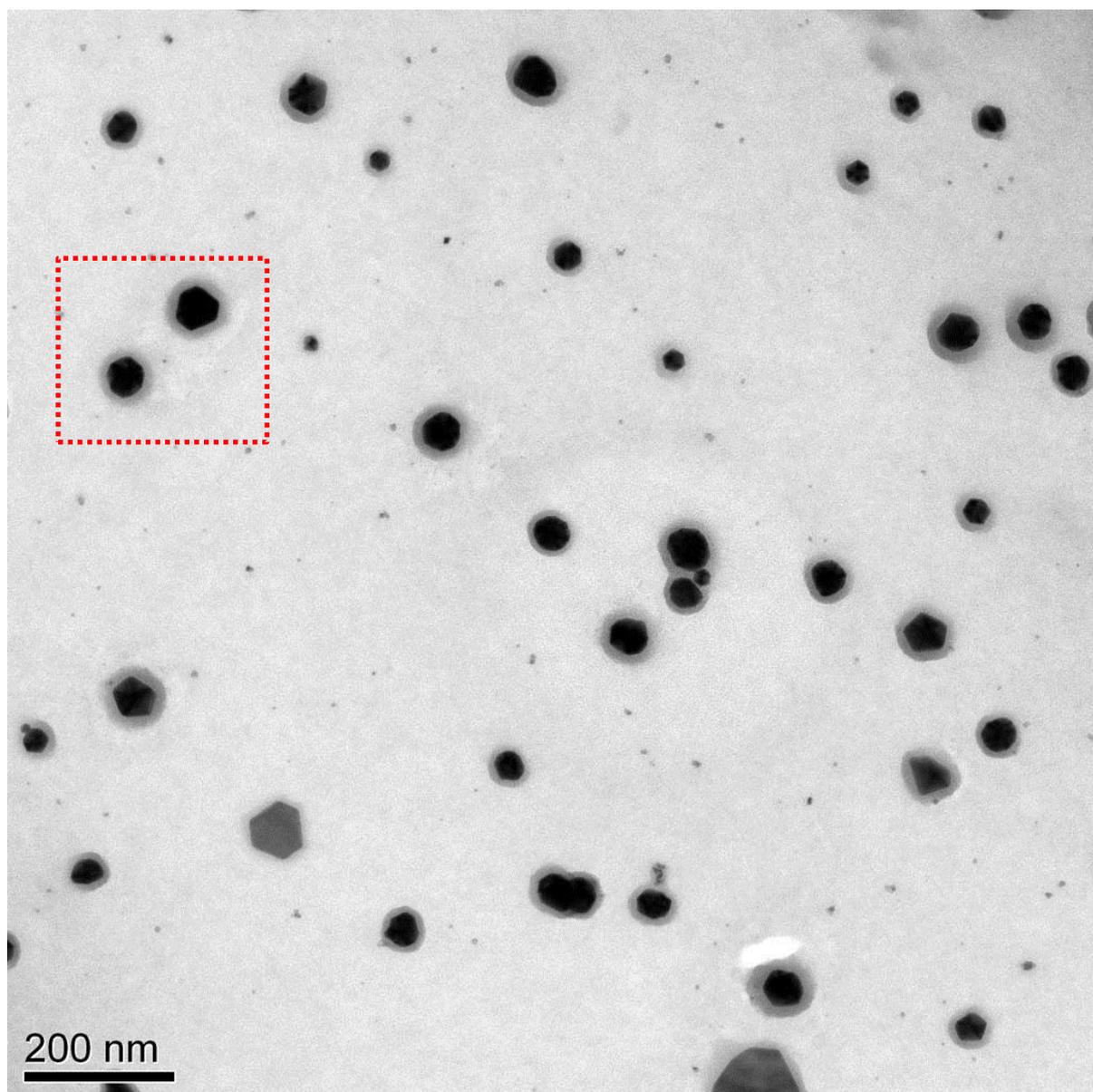
Figure S2 Showing distinct Au@Pd core-shell nanoparticles observed over the sample grid. Nanoparticles observed in the highlighted region were further subjected to STEM analysis.
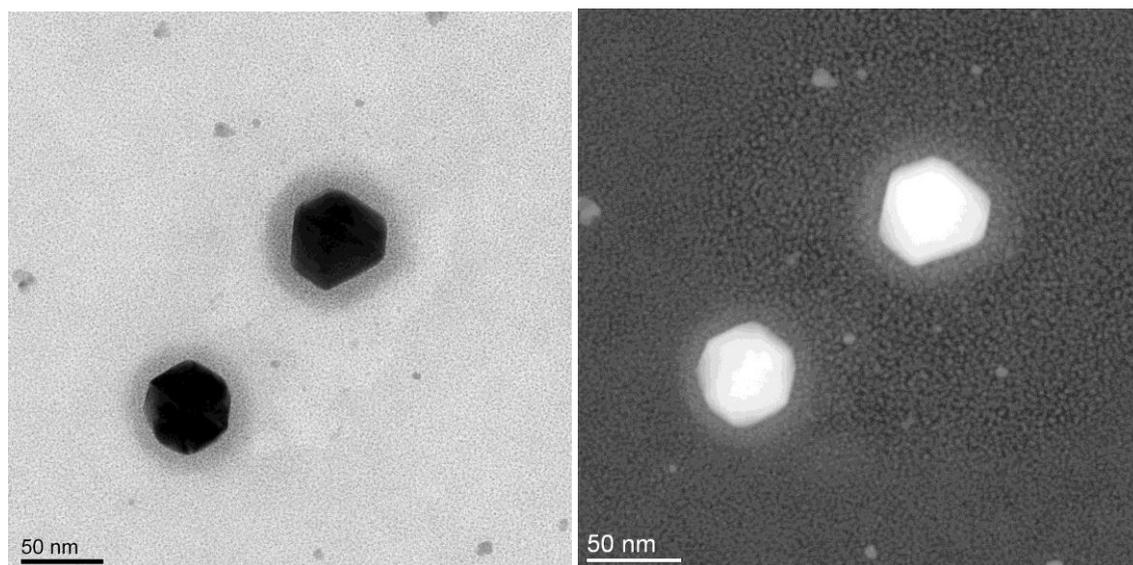
Figure S3 (L to R): Au@Pd nanoparticles as observed by HRTEM and STEM respectively.
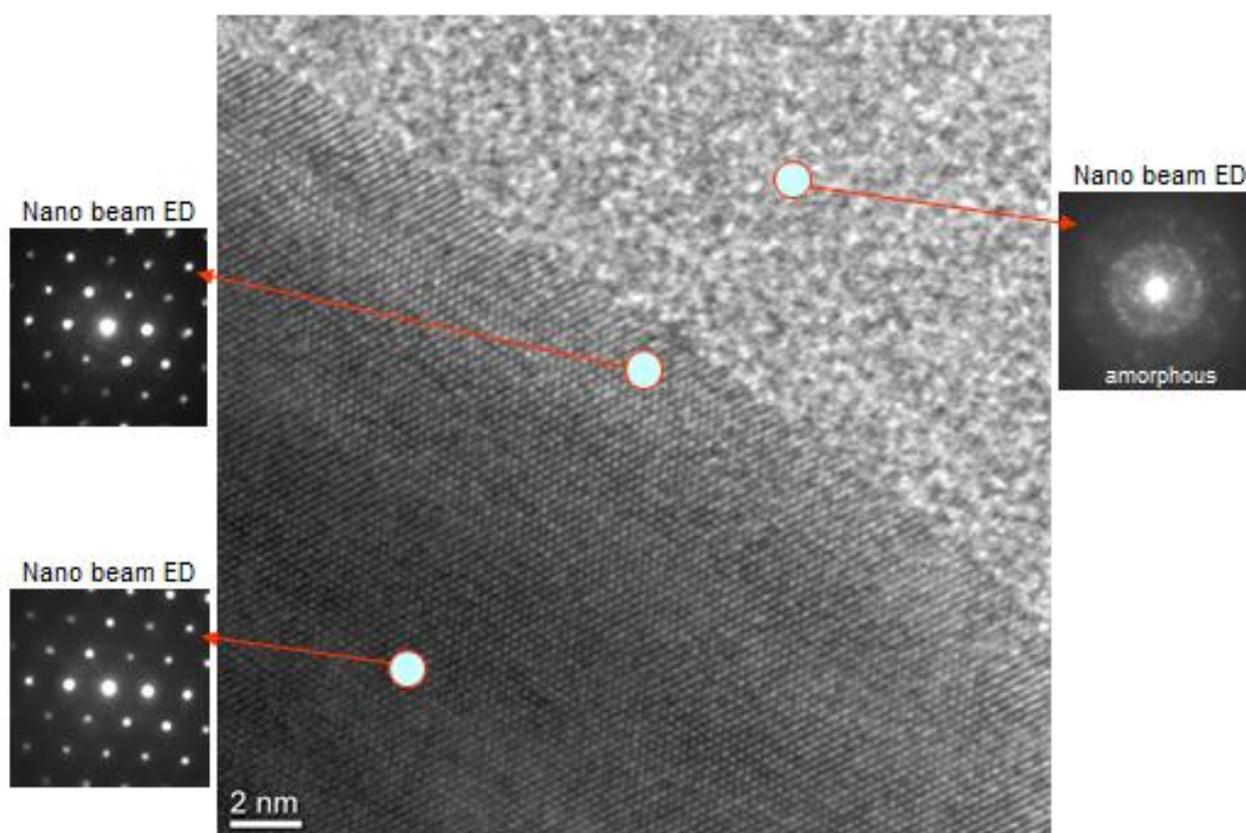
Figure S4. Showing the boundary layer observed in Au@Pd nanoparticles. The Au core was highly crystalline (Au 111) as compared to largely amorphous Pd shell. It is interesting to note that although, some atoms in the Pd layer are supposed to be crystalline supposedly near the surface boundary of Au@Pd.
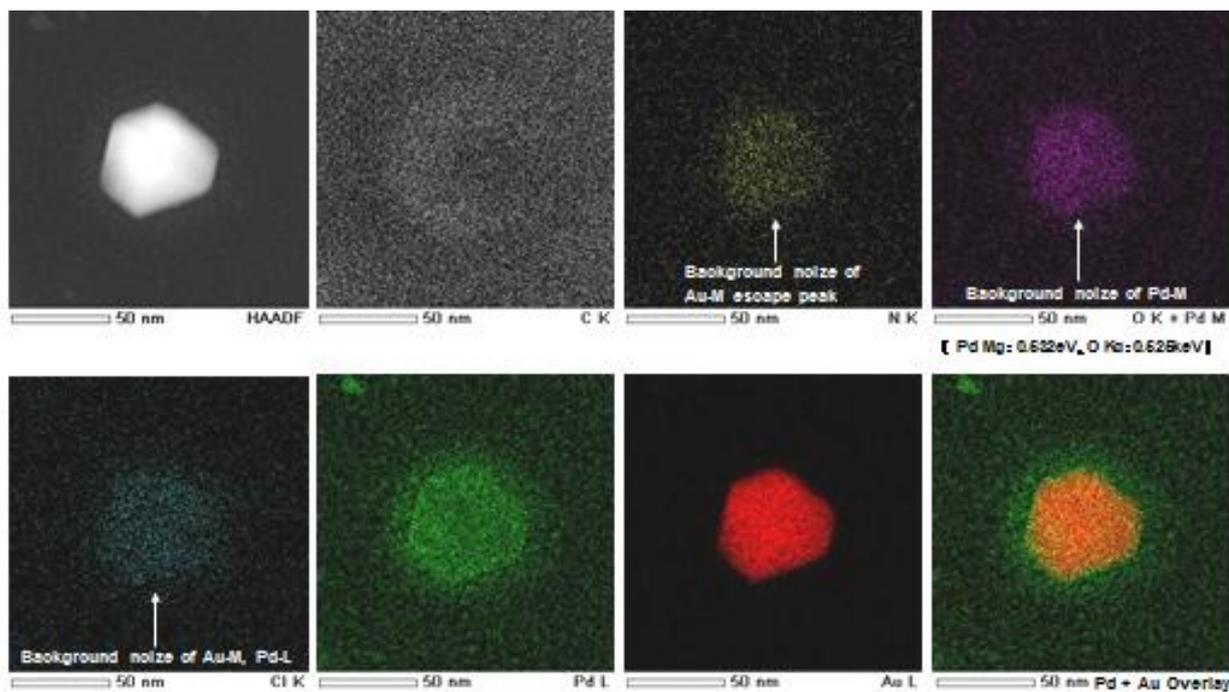
Figure S5. Shows elemental scanning obtained by STEM-EDX confirming the majority core comprising of Au atoms while shell is that of Pd.
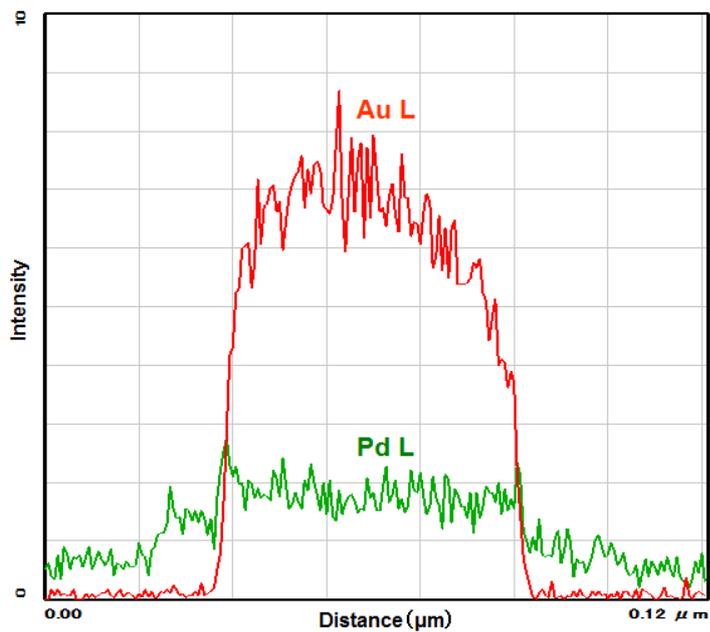
Figure S6. Showing the intensity line profile of Au@Pd nanoparticle confirming core-shell morphology (on the absence of distinct Pd peak)

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2.   Au, Pd and Au@Pd NP catalytic efficiency in degradation of 4-Nitrophenol.

Au@Pd bimetallic nanoparticles with core-shell morphology in particular have proved to be excellent catalysts for a variety of reactions including oxidation reactions which are of importance in field of fuel cells, semiconductors, drug delivery and so on. These nanoparticles upon being adhered to a matrix, may serves as a better catalyst than bulk metal due to greater accessibility to surface atoms and low coordination number especially in case of water treatment. Among several water pollutants, nitroaromatic compounds are considered as the most toxic and refractory pollutants whose permissible range is as low as 1 to 20 ppb. However, these are common in production of dyes, explosives, pesticides among many others and thus their industrial production is considered as an environmental hazard. Upon being released into the environment, these nitrophenols pose significant public health issues by exhibiting carcinogenic and mutagenic potential in humans. Thus, there is a need to develop cost-effective methods for removing nitroaromatic pollutants from water by utilizing these catalytic nanoparticles.

Preparation of nanoparticle based catalyst in degradation of 4-Nitrophenol

The reduction of 4-NP by $NaBH_4$ was studied as a model reaction to probe catalytic efficiency of Au, Pd and Au@Pd catalyst for heterogeneous systems. Under the experimental condition, reduction does not proceed at all simply with addition of $NaBH_4$ or biomass alone. But in presence of catalyst coated glass beads, it proceeds to completion with formation of 4-Aminophenol (4-AP). To study the reaction in a quartz cuvette, 2.77 mL water was mixed with 30 µL (10^{-2} M) 4-NP solution and 200 µL of freshly prepared $NaBH_4$ (10^{-1} M) was added. Catalyst coated glass beads were prepared by modified protocol of Shen et el. (Langmuir 2012, 28, 7519). Porous glass beads were prepared by autoclaving the glass beads (2 mg) in water (100 mL) at 121 °C for 2 hours. Afterward, the reactor was cooled to room temperature through natural cooling. Eventually, the porous glass beads were and washed several times with deionized water before further use. A total of 20 mg of these glass beads was added to Au, Pd and Au@Pd nanoparticle solution (5 mL) stated previously. The nanoparticle loading of around $2x10^{-3}$ g/L was introduced into the reaction cuvette.

The mixtures were stirred for 12 h at 60° C to evaporate the solvent (water). These nanoparticle coated glass beads were then dried at 90°C for 24 hours. UV-Vis spectra of the 4-NP sample were recorded at every 2 min interval in the range of 200-600 nm. The percentage degradation of 4-NP was determined by measuring the change in absorbance of the initially observed peak at 400 nm, for the nitrophelate ion as the function of time.

Finally, catalytic activity of Au, Pd and Au@Pd NPs were tested by oxidation of 4-Nitrophenol. Both Au and Pd NPs have found tremendous catalytic usage as described previously but not Au@Pd bimetallic NPs in degradation of nitroaromatic pollutants. Aqueous 4-NP shows maximum UV-Vis absorbance at 317 nm [Pradhan et al. Langmuir 2001, 17, 1800]. When NaBH4 (pH>12) was added to reduce 4-NP, an intense yellow color appeared due to formation of 4-nitrophenolate ion red-shifting the absorption peak to 400 nm [Ghosh et al. Appl. Catala. Gen. 2004, 268, 61]. The reaction does not proceed and the peak remained for several days in absence of catalyst [Hayakawa et al. Langmuir 2003, 19, 5517; Pradhan et al. Colloid Surface A 2002, 196, 247].

Normally, -NO$_2$ containing aromatic compounds are inert to the reduction of NaBH$_4$. But, with the addition of glass bead coated nanoparticles, the color faded to a colourless solution and the peak at 400 nm decreases with the extent of reaction time. Au, Pd and Au@Pd NPs coated over the glass beads helped in transfer of electron from BH$_4^-$ ions to nitro group of 4-NP and reducing it to 4-AP, which was qualitatively monitored by UV-Vis spectroscopy as shown in figure 6b. Since, the concentration of catalyst coated glass beads catalysing the reaction was very low, measurement of the absorption spectra of 4-NP and its subsequent reduction into 4-AP, was not disturbed by the light scattering due to the catalyst carrier particles in the reaction mixture. We compared the degradation potential (figure S7) of Au, Pd and Au@Pd nanoparticles coated glass beads under same reaction condition to give us an idea about their efficacy in heterogeneous catalysis.
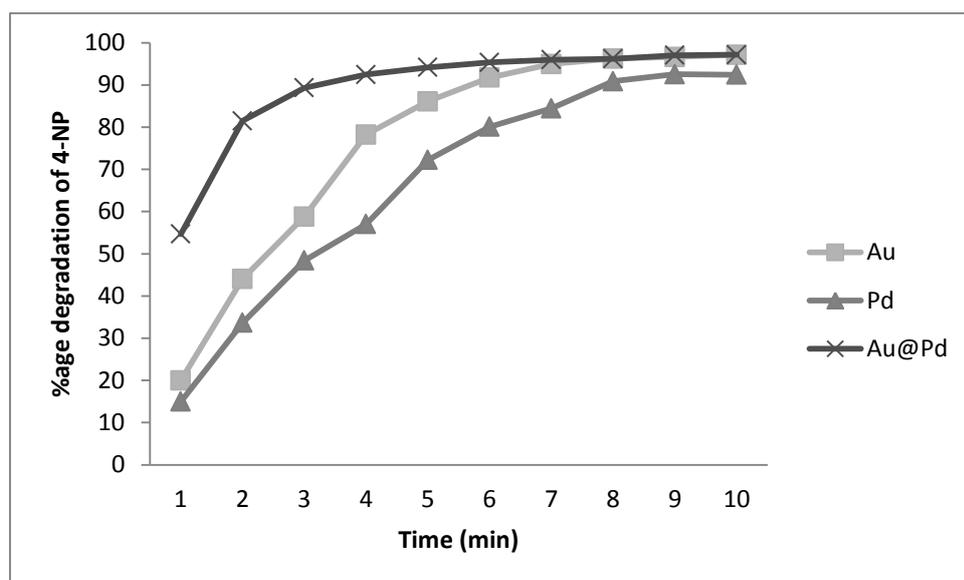
Figure S7. Showing percentage degradation of 4-Nitrophenol by Au, Pd and Au@Pd nanoparticle coated glass beads.

Au@Pd bimetallic nanoparticles proved to be a very efficient catalyst in degradation of 4-NP as compared to Au and Pd NPs coated over glass beads. In the first sixty seconds of the reaction, Au@Pd coated glass beads degraded about 55% of 4-AP as compared to 20% and 15 % by Au and Pd NPs respectively. At the end of 5 minutes, Au@Pd NPs degraded 94% of 4-AP as compared to 86% and 72% by Au and Pd NPs respectively. However, at the end of reaction at 10 minutes, all the three coated NPs showed similar results with Au and Au@Pd as 97% while Pd as 92%. This intense catalytic activity of Au@Pd bimetallic nanoparticles exceeded than that of individual metal NPs (Au and Pd). In fact this increased activity by bimetallic system arises due the synergistic effect between Au and Pd which is well-recognized phenomenon in liquid phase oxidation [Enache et al. Science 2006, 11, 362; Dimitratos et al. Catal. Lett. 2005, 9,181]. It is interesting to note that while Pd NPs alone were amorphous in nature, they were rather poor in oxidation of 4-NP. However, in case of Au@Pd NPs the interfacial layer containing crystalline Au and Pd crystals greatly improved the degradation potential. This preliminary study clearly demonstrates effective catalytic activity in all the three types of nanoparticles (Au, Pd, Au@Pd NPs) synthesized via Trp in aqueous environment.

Finally, it should be noted that the reduction rate of 4-NP can be influenced by the concentration of catalyst, size of catalyst, concentration of reactants and temperature [Panigrahi et al. J Phys. Chem. C 2007, 111, 4596]. Although there may be a few drawbacks like polydispersity of nanoparticles which may affect the catalytic potential, nonetheless considering the economic viability and facile green synthesis, this study helps in better understanding of bimetallic nanoparticle synthesis and its associated application for the reduction of nitroaromatic pollutants.