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# Colloidal design of Au@Pt nanoflowers with good catalytic activity and SERS investigations on river soil

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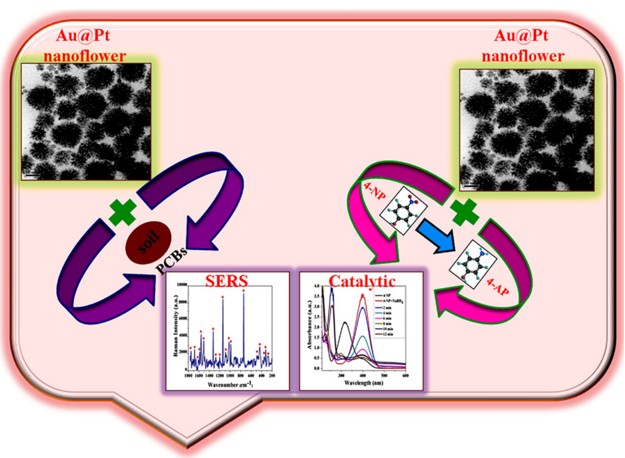
## GRAPHICAL ABSTRACT




## ARTICLE INFO

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## ABSTRACT

A novel and fresh Au@Pt nanoflower synthesised by the chemical reduction method. Au@Pt nanoflowers exhibit the Au SPR peak at 530 nm and the peak of Pt NPs at 265 nm. Transmission electron microscopy (TEM) analysis showed the average particle size to be 19 nm. Using Surface Enhanced Raman Scattering (SERS) the pollutants such as Poly Chlorinated Biphenyls (PCBs) were detected in the real environmental sample; river soil and it is further confirmed through Gas Chromatography and Mass Spectrometry (GC–MS) studies. The catalytic activity of Au@Pt nanoflowers was studied via the catalytic reduction of 4-nitrophenol (NP) to 4-aminophenol (AP) assisted by $NaBH_4$. Au@Pt nanoflowers exhibit the highest catalytic activity, converting 4- NP to 4- AP in 12 min.

## 1. Introduction

Polychlorinated biphenyls (PCBs), a class of conspicuous persistent organic pollutants (POPs), have been widely used as industrial oil additives, coolants and some consumer products [1]. They were found to be high toxic to humans through the food chain accumulation and mutagenic by interrupting hormones in the body [2,3]. Although the production and usage of PCBs have been banned by the United States

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Congress in 1979 and the Stockholm Convention on POPs in 2001, they can still be identified in air, water, soil, aquatic life, and even in human adipose tissue due to their world-wide transferability and bioaccumulation [4,5]. Recently, the technique used for detecting the PCBs is high-resolution gas chromatography and mass spectrometry (GC–MS). Initially, analytical tests looked for chromatographic patterns that signified different manufacturers' PCB blends. As it became more significant to classify the PCBs based on their toxicity rather than their origin, the ability to detect and identify individual PCB congeners became necessary [6]. A new technique is demanded for the fast detection of PCBs.

SERS analysis has developed into a noteworthy tool in assorted fields such as analytical chemistry, environmental monitoring, forensics and biology due to its SPR in nanostructured metal surfaces [7]. Suitable substrates for SERS analysis are most desirable. Nanomaterials expose many interesting properties and use to find the detection of organic pollutants [8]. For example, some organics were detected by SERS in trace amounts, using noble metal (Au, Ag, and Cu) nanomaterial as the substrate [9]. Au NPs exhibit enhanced optical interaction with visible light because of the so-called LSPR, which can be suitable to the development of new chemo sensors. In this investigation our motivation and interest in preparing core-shell Au@Pt nanoflower can be used as an excellent SERS-active substrate. The Au@Pt nanoflower had high reliability and good tolerability. Pt-on-Au bimetallic nanoparticles (NPs) exhibited more obvious advantages because of the SPR property and higher chemical stability [10]. An effective and sufficient way to obtain SERS-active metal surfaces was to prepare core-shell bimetallic NPs. With the help of the electromagnetic (EM) enhancement created by the SERS-active substrate underside, SERS spectra of adsorbates on the transition metal overlayer could be obtained. Moreover, SERS activity also depended on both the size and the shape of the NPs. The nanometre-scale surface roughness of branched nanometals provided hot spots on a single particle, which significantly enhanced SERS effect [11,12].

Water pollution is caused by overuse of dyes in textile, pharmaceuticals & pesticides industries, which discharge many nitro aromatic compounds into the water system. 4-NP is the most toxic of the nitro aromatic compounds [13]. Many methods have been developed to solve the pollution problems caused by 4-NP. Currently the conversion of 4-NP into 4-AP by the method of catalytic reduction has attracted much attention, due to its high conversion efficiency and uncomplicated operating conditions. Au NPs can play an important role in the reduction of 4-NP. But Au NPs are usually unstable since they grow into larger particles during the catalytic reduction reaction [14]. This drawback can be overcome by incorporating with Au NPs by other metal NPs [15]. Bimetal can also act as a physical barrier that prevents aggregation of Au NPs. Moreover, the bimetal is subject to reduction processes which can participate directly in the catalysis by providing intermediate products to Au, such as $O^2$ &. H, and thereby speed up the process of catalytic reaction. Among bimetallic NPs, Pt-Au bimetal catalyst is favoured because of its promising use in the selective hydrogenation of aldehydes, olefins and nitro aromatics. The addition of Pt NPs is suggested in this work, to promote the dissociation of $H_2$ and enhance the activity of the reduction. Motivated by the urgent demand, in this work to detecting PCBs and identifying the isomers of PCBs by using SERS technique with core shell Au@Pt nanoflower as a substrate on river soil. Also the prepared core shell Au@Pt nanoflower expose faster catalytic activity towards the reduction of 4-NP and expected to be invested as a highly efficient catalyst for many applications.

## 2. Experimental

### 2.1. Materials

Hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$, 98%), sodium borohydride ($NaBH_4$, 95%), sodium citrate ($Na_3C_6H_5O_72H_2O$, 99.5%), Potassium tetrachloroplatinate ($K_2PtCl_4$, 98%), Ascorbic Acid (AA, 99%), polyvinylpyrrolidone (PVP, 98%) were purchased from MERCK. All the chemicals were of analytical grade and were used as purchased without further purification. Double distilled water was used throughout the experiment.

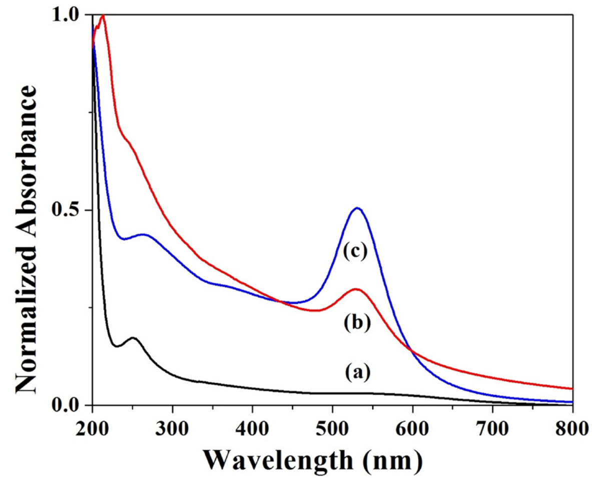


**Fig. 1.** Optical absorption spectra of (a) Pt NPs, (b) Au NPs and (c) Au@Pt nanoflowers.

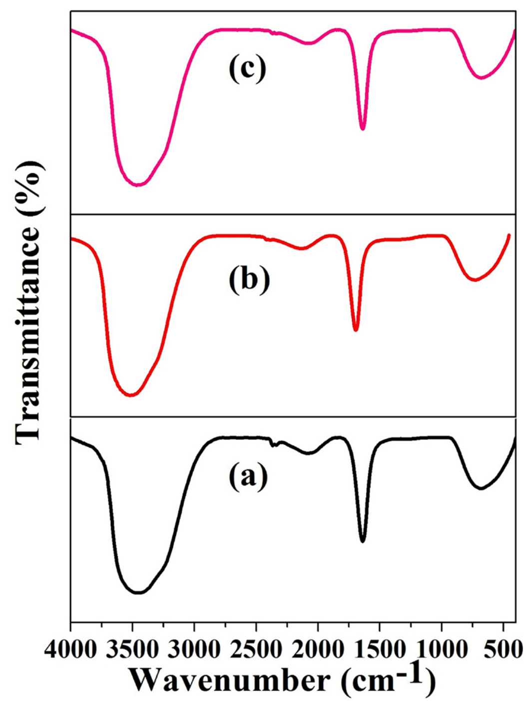


**Fig. 2.** FTIR spectra of (a) Pt NPs (b) Au NPs and (c) Au@Pt nanoflowers.

### 2.2. Soil sample preparation

The soil sample was acquired from the river (Kodaikanal, TamilNadu). It was dried and made into powders using mortar and pestle. 0.20 g of powdered soil sample was dissolved into 20 mL acetone. It was stirred for 5 min. This suspension was allowed to precipitate for 30 min at room temperature. The supernatant solution of soil extract was used for investigation.

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