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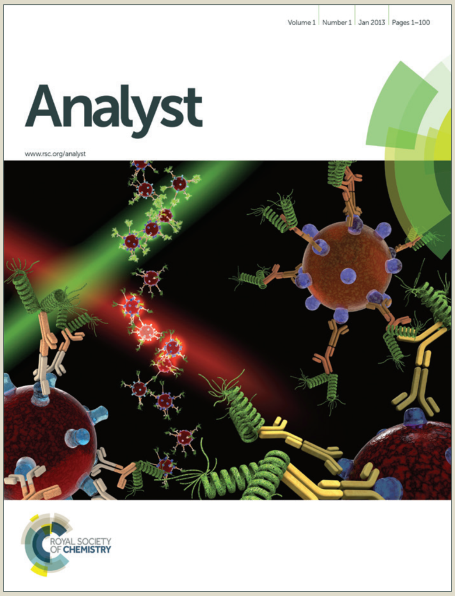

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Communication

Newly made observation in seed-mediated approach and its application for highly selective rapid naked eye detection of mercury (II)

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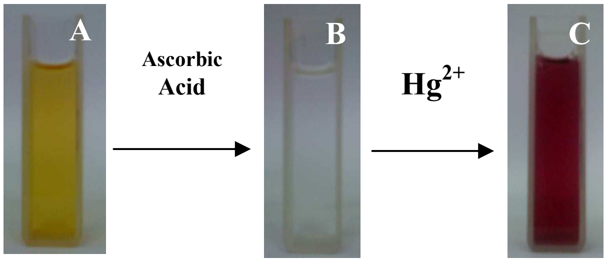
We report, novel seedless Hg^{2+}-induced synthetic approach for the preparation of gold nanostructures. This protocol is demonstrated for a highly selective and sensitive naked eye Hg^{2+} detection based on high affinity metallophilic Hg^{2+}-Au^{+} interaction. The response time upon exposure to Hg^{2+} is almost instantaneous.

Several methods on the synthesis of gold nanostructures are reported for a variety of applications, including biological imaging, sensors, surface enhanced Raman spectroscopy, drug delivery, biomoecule detection and photothermal therapy of cancer cells[1-10]. Among the available methods, *"seed mediation"* is the most widely employed to synthesis different aspect ratio of nanorods, as reported by C.J. Murphy et al.[11] Seed-mediated methods are ofcourse, employed to prepare gold nanostructures with different size and morphology such as nanowires, nanostars, nanospheres, nanoprisms, etc.[12-15] Here, a mixture of auric chloride ($HAuCl_4$), cetyltrimethylammonium bromide (CTAB) and ascorbic acid (AA) leads to the formtion of Au(I) in aqueous solution. This is reasoned as, ascorbic acid is a weak reducing agent, hence partial reduction [Au(III) to Au(I)] is favoured in the presence of high concentration of CTAB and in the absence of a seed, as evidenced by the nonexistence of a gold plasmon band[16]. Edgar et al. reported, Au(I) ion in the growth solution are not reduced to Au(0) even when an excess of (~ 5 molar equivalent) ascorbic acid addition. The reduction of Au(I) to Au(0) is possible only upon the addition of gold nanoparticle seed[17]. Not only by these two groups, other researchers are also reported that it is not possible to reduce Au(I) to Au(0) without gold nanoparticle seed. On contrary, we have demonstrated the generation of gold nanostructures without the addition of any seed material. Further, this approach is exploited for the selective and sensitive naked eye rapid detection of trace level mercury ion in water samples.

Detection of mercuric ion in water samples is a serious concern because of its harmful effects on the environment and human health.[18] In the past, several optical sensor systems has been developed based on biomolecules[19], DNAzymes[20] and gold nanoparticles functionalized with various labels (e.g. DNA).[21, 22] However, most of the reported methods are instrument based, which make them complicated for field analysis. There is a vast interest to develop a simple and label-free method that has improved characteristic, together with cost, speed, ease, sensitivity, selectivity, compatibility and miniaturization. In addition, these systems are incompatible with aqueous environment and not suitable for on-site environmental monitoring.

It is of interest for simplicity, to develop a reliable method for the detection of mercuric ion by naked eye using a specific and strong interaction like Hg^{2+}-Au^{+}. Recently, Pyykko et al mentioned that the dispersion forces between the closed-shell metal atoms are extremely specific and strong. The interactions involved in the heavy ions such as Hg^{2+} and Au^{+} can be significantly magnified by relativistic effect [23]. In addition, J. Xie et al [24] reported highly selective and ultra sensitive detection of Hg^{2+} based on fluorescence quenching of gold nanoclusters by Hg^{2+}-Au^{+} interactions. Here, it is pointed out that the surface of the cluster is stabilized by a small amount of Au^{+} (~17%) that should have strong interactions with Hg^{2+}. In this basis, the Hg^{2+}-Au^{+} interaction chemistry is more eye-catching for mercury detection. Therefore, in this work, attempts were made to prepare Au^{+} in aqueous solution exploiting Hg^{2+}-Au^{+} interaction chemistry to develop a simple, sensitive and highly selective rapid naked eye detection of mercury (II).

Here, $HAuCl_4$ and CTAB are mixed together that resulted in orange-yellow colour. Afterwards, ascorbic acid is added to this solution, where the orange-yellowish colour immediately becomes colourless. When mercury ions are added, it turns instantaneously to wine-red colours that indicate the formation of gold nanoparticles as shown in scheme-1.



Scheme 1: (A) CTAB + $HAuCl_4$; (B) addition of ascorbic acid; (C) addition of Hg^{2+}

UV-Vis absorbance spectrum of the reaction sequences are shown in Fig 1. The $HAuCl_4$ solution shows an absorbance peak at 300 nm, which is due to the ligand metal charge transfer. When

CTAB is mixed with $HAuCl_4$ solution, the absorption peak shifted to 400 nm which are close to $AuBr_4^-$ peaks. This change is caused by the ligand exchange from Cl^- to Br^-. The net reaction between the $HAuCl_4$ and CTAB in aqueous solution, results in the formation of [CTA]-[$AuBr_4$]. When ascorbic acid is added to this solution, the absorption peak is completely disappeared. This could be reasoned as the formation of organic salt complex [CTA]-[$AuBr_4$], which is solubilised using surfactant micelles to produce "metallomicelles". This is further evidenced from the potential measurement of the Au complex [$AuBr_4^-$], which is lower (0.805 V) than that of Au (III) ion (1.40 V). Moreover, in the growth solution, $AuBr_4^-$ exists as CTA-$AuBr_4^-$ which is expected to be more stable one. Therefore, the nucleation can be suspended and ascorbic acid reduces the $AuBr_4^-$ in the metallomicelles to $AuBr_2^-$. Alternatively, when Hg^{2+} is added into the Au^+ solution Au^+ to Au^0 reduction takes place that leads to the formation of different shapes of gold nanostructure, which is confirmed by the appearance of new absorption peak at 520 nm.

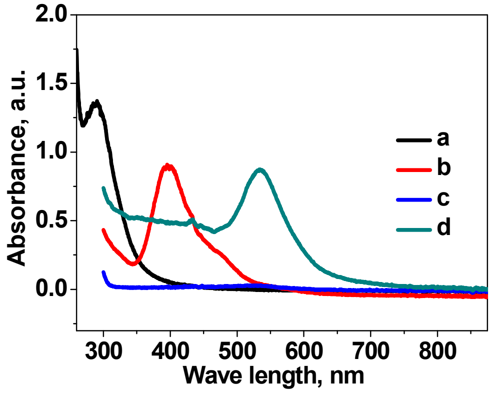


Fig. 1: (a) $HAuCl_4$ alone; (b) $HAuCl_4$ + CTAB; (c) $HAuCl_4$ + CTAB + AA; (d) $HAuCl_4$ + CTAB + AA + Hg^{2+}

The overall mechanism of the reduction process may be described as:

$$AuCl_4^- + 4\,CTAB \rightarrow CTA\text{-}Au^{III}Br_4^- + 4\,Cl^- + 3\,CTA^+$$

Orange yellow colour

First reduction: Au^{III} to Au^{I}

$$CTA\text{-}Au^{III}Br_4^- + C_6H_8O_6 \rightarrow CTA\text{-}Au^{I}Br_2^- + C_6H_6O_6 + 2H^+ + 2Br^-$$

Colourless

Second reduction: Au^{I} to Au^{0}

$$2CTA\text{-}Au^{I}Br_2^- + C_6H_8O_6 \xrightarrow{Hg^{2+}} 2\,Au^0 + C_6H_6O_6 + 2CTA^+ + 2H^+ + 4Br^-$$

Wine-red colour

In this mechanism, the second reduction process may be reasoned as, Hg^{2+} ion induces the conversion of Au^+ into Au^0 because the recent theoretical studies predict that the dispersion force between the closed-shell metal atoms or ions are highly specific and strong especially these interactions involve heavy ions such as Hg^{2+} ($4f^{14}5d^{10}$) and Au^+ ($4f^{14}5d^{10}$)[23-24]. Therefore, Au^+ ions are reduced to Au^0 due to the disproportionate reaction of Au(I) induced by Hg^{2+} which is similar to the seed mediated approach where the disproportionate reaction of Au(I) is catalysed by metallic gold seed[17].

$$3\,Au^{I} \rightarrow 2Au^0 + Au^{III}$$

Fig.2. shows the TEM image and the corresponding selected area electron diffraction pattern of the gold nanostructures. Various shapes of gold nanostructures such as spherical, rod, triangle, and hexagonal shapes are observed. To obtain the specific shape of interest for e.g., only spherical, or rod or wire or chain, the $HAuCl_4$ and ascorbic acid ratio is varied i.e., 1:2, 1:5, and 1:10 respectively.

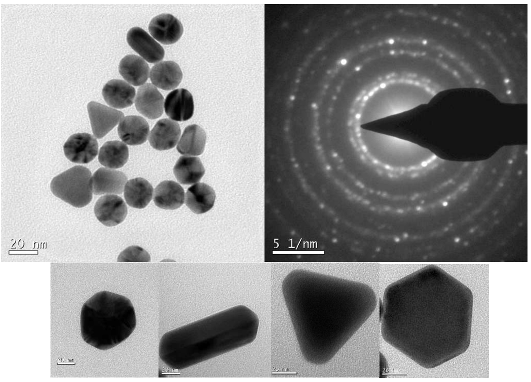
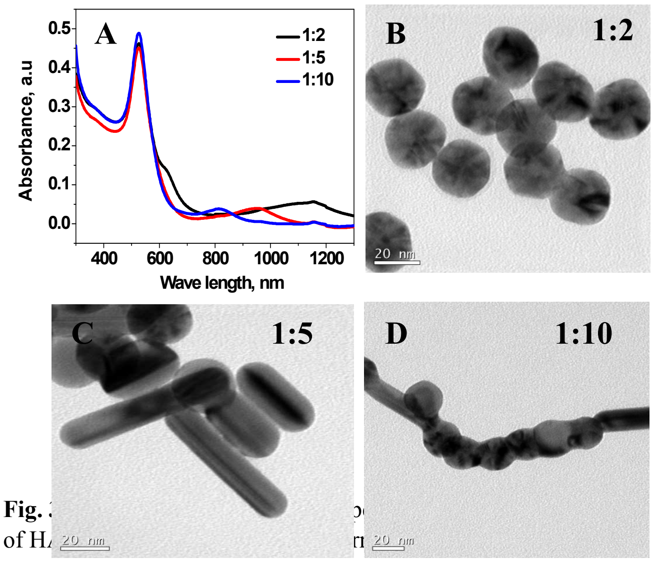


Fig. 2: TEM images and the corresponding SAED pattern of the synthesized gold nanostructures.

The UV-Visible absorbance spectrum of the gold nanostructures synthesized at different ratio, such as 1:2, 1:5 and 1:10 and the corresponding TEM images are shown in Fig.3. The UV-visible and the TEM images clearly signify the presence of spherical and anisotropic gold nanostructures. The first absorbance band at around 520 nm (Fig.3A) is observed for all these ratios; due to the presence of spherical gold nanostructure. However, for 1:2 ratio, it is observed mostly spherical gold nanostructure as shown in Fig.3B. In addition, a small absorbance band appeared at around 600 nm & 1180 nm for 1:2 ratio is due to the presence of few anisotropic nanostructure in the synthesized colloids which is also shown in the low magnification TEM image (Supporting Information, Fig.S1). While 1:5 and 1:10 ratio showed the second absorbance bands around 970 nm and 800 nm respectively is due to the presence of nanorod and nanochain structures as shown in the TEM images of Fig. 3C and Fig. 3D respectively. This is because; gold nanorods are well-known for their unique optical property which arises from the localized surface plasmon resonance (LSPR). This is generated by collective oscillations of conduction band electrons upon illumination with light, while spherical particles absorb light only in the visible region. Anisotropic particles possess a second absorption band, the so-called longitudinal absorption band. The position of the latter strongly depends on the aspect ratio of the nanorods and can be shifted towards the near-infrared region and beyond which the aspect ratio increases. Hence, the preliminary results indicate the possibility of synthesising various types of gold nanostructures such as spherical, rod, and chain just by varying the ratio between the auric chloride and ascorbic acid using the present approach with very small amount of Hg^{2+} ion (ppb level). The proposed method is very simple and fast (few minutes) compared to the previous seed-mediated method (overnight)[25].



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The gold nanostructure synthesised at 1:5 ratio using Hg^{2+}-induced synthetic approach is exploited for the naked eye detection of trace level of Hg^{2+} ion and is shown in Fig.4. To estimate the sensitivity assay, different concentration of mercury ion (from 0-1000 nM), are introduced to a series of solutions containing Au^{+}, which is colourless. The colour of the Au^{+} solution instantaneously changed into blue, pink or wine-red depends on the mercury ion concentration. This is because of the strong interaction between the Hg^{2+} and Au^{+}. Hence, by naked eye itself one can clearly detect the Hg^{2+} presence at nanomolar level (LOD = 10 nM), which is very lower than the reported methods.[26-30]

Fig.4: Colour developed by the addition of mercury ion (0-1000 nM) into Au^{+} colourless aqueous solution

To ascertain the selectivity of this method, Hg^{2+} is detected in the presence of other common interfering metal ions. Fig. 5 clearly portrays the Au^{+} solution colour does not change even, ten times of higher concentrations (100 µM) of the other metal ions such as Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Ag^{+} are introduced in the solution. The colour of the solution changed to wind-red colour only in the presence of Hg^{2+} ion (10 µM) that shows the excellent selectivity of this present approach which could be witnessed with the naked eye.

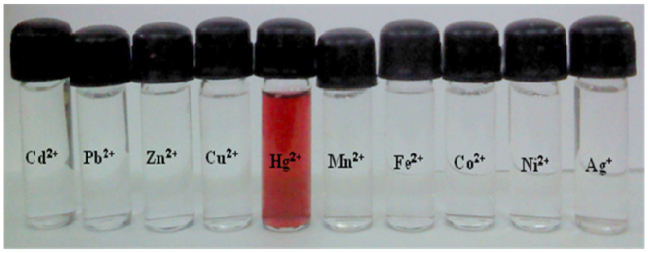

Fig.5: Selectivity of the rapid naked eye detection of mercury ion (10 µM) and other metal ions (100 µM)

In summary, we have demonstrated the synthesis of gold nanostructure using novel seedless Hg^{2+}-induced synthetic approach for the first time. In addition, we also explored the possibility of synthesising various shapes of gold nanostructures like spherical, rod, triangle, hexagonal and wire/chains by simply changing the $HAuCl_4$ and ascorbic acid ratio. The present methodology showed a very high selectivity even in the presence of other metal ions and also detecting Hg^{2+} ion concentration as low as 10 nM by naked eye itself. Hence, the proposed method is simple, label-free, sensitive and highly selective for the rapid naked eye detection of trace level mercury ion based on Hg^{2+}-Au^{+} interaction. Thus, the novel observation may open a new way to explore further worldwide.

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Table of contents

Highly selective & sensitive naked eye detection of Hg^{2+} achieved based on Hg^{2+}-Au^{+} interaction and observed Au^{I} to Au^{0} in absence of seed.