



## Research paper

# Aggregation induced, formaldehyde tailored nanowire like networks of Cu and their SERS activity

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## HIGHLIGHTS

- Simple wet chemical procedure was demonstrated to obtain nanowire like Cu nano-networks.
- Non-toxic, common organic molecule formaldehyde was used as reducing agent.
- Cu nano networks containing interesting inter-particle junctions can act as “hotspots”.
- SERS activity of these structures was examined by methylene blue as analyte molecule.

## ARTICLE INFO

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## ABSTRACT

Low cost SERS substrates are imperative to develop single use, point of care diagnostics. In the quest for such SERS substrates, we developed a wet chemical method to produce Cu nanowire like networks. The oriented attachment and coalescence observed in these network like nanostructures infer their aggregation behavior that ultimately results in the generation of exciting inter-particle junctions. The hot spots formed by these inter-particle junctions certainly increases the electromagnetic enhancement. SERS activity of these substrates is evaluated using methylene blue (MB) molecule and found activity enhancement by a factor of  $1.1 \times 10^4$ .

## 1. Introduction

Surface enhanced Raman scattering (SERS) evolved as a powerful analytical tool in the trace level detection of several compounds using coinage nanoparticles as SERS substrates [1,2]. SERS enhancement takes place by two phenomena viz. chemical and electromagnetic enhancements. Further, electromagnetic enhancements are known to give higher order enhancement factors than chemical enhancements. Surface plasmons possessed by coinage metal nanoparticles are shown to improve the Raman signals by electromagnetic enhancement. Among the coinage metals, Ag is well established and most suitable SERS substrate to get high enhancement factors (EFs). Nevertheless, the current need in point of care diagnostics demand single use, low cost SERS substrates [3,4]. Fabrication of such type of single use SERS substrates using Ag is not viable. Hence the other low cost, earth-

abundant coinage metal Cu needs to be explored as an alternative SERS substrate to silver.

Fabrication of Cu based SERS substrates are mainly focused on the immobilization of Cu nanoparticles on various substrates by physical methods. Pereira *et al.* fabricated Cu nanostructures on borophosphate glasses and achieved promising EFs of order  $10^7$ – $10^8$  for Rhodamine B [5]. A 3D PDMS microfluidic channel in which Ag nanoparticles deposited on Cu micro particles was used as SERS substrate for methylene blue (MB) molecule by Zhang *et al.* [6]. Pulsed laser ablation technique was used to fabricate Cu/C<sub>3</sub>N<sub>4</sub> SERS active substrates and examined on crystal violet (CV), methylene blue (MB) and rhodamine 6G (R6G) molecules to achieve the enhancement factor of  $10^7$  [7]. Muniz-Miranda *et al.* fabricated SERS active Cu nanocolloids by laser ablation method [8]. Electrochemically deposited Cu substrates were used as SERS substrates for R6G molecule by Yang and co-workers [9]. Xu *et al.*

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fabricated multifunctional Cu mesh and it is used as SERS substrate for the detection of dye molecules [10]. Cu nanoparticles grafted on silicon wafers were used as SERS substrates by Shao *et al.* using R6G molecule [11]. He *et al.* described fabrication of hierarchical Cu/ reduced graphene oxide (rGO) SERS substrate for R6G [12]. Cu/rGO was also synthesized by Guo *et al.* for SERS detection of CV [13]. Cu nanoparticle array was fabricated by ion sputtering method using polystyrene molecules as templates for SERS activity of CV and 4-aminothiophenol [14]. Co-sputtering and dealloying techniques were employed to fabricate Cu nanofilm SERS substrates for R6G by Diao *et al.* [15]. Besides all these physical methods to fabricate Cu based SERS substrates, Cu containing bimetallic/alloy nanostructures were also used as SERS substrates. Singh *et al.* used intermetallic of Au-Cu as SERS substrates for the detection of MB [16]. Ag decorated Cu nanoparticles were fabricated by He *et al.* used for the real time SERS monitoring of degradation of R6G and dimerization of 4-nitrothiophenol [17]. Ag-Cu alloy nanoparticles were fabricated by laser ablation techniques and used for detection of explosives by Bharati *et al.* [18].

All these methods described so far summarize the fabrication and use of Cu based SERS substrates either by physical methods or by its alloys. Although wet chemical methods to synthesize nanoparticles are known to have great control over the product formed, fabrication of Cu SERS substrates by wet chemical methods are sparse in literature. For instance, Mao *et al.* described a wet chemical colloidal route to synthesize Cu nanoparticles and it is used for the SERS detection of CV with an EF of  $10^3$  [19]. Rao *et al.* synthesized highly porous 3D Cu leaves by wet chemical route using toxic hydrazine which could give a EF of order  $10^4$  with 1 mM R6G [20].

As discussed earlier, the wet chemical processes have good control over the shape and size of the nanoparticles which enable them superior to the other methods. But the existing Cu nanoparticles synthesis by wet-chemical procedures involve the use of toxic reducing agents [21,22] and very long chain surfactants [23] that could obstruct the interaction of analyte molecules with nanoparticle surfaces for SERS applications. Therefore, a strong necessity arises to look for more efficient wet chemical methods and it would also be interesting and expedient if the synthetic methods could generate the nanostructures with inter-particle junction to form “hot spots” for SERS applications. In this regard, we describe a simple, toxic-free wet chemical process to produce Cu nanostructures using formaldehyde as reducing agent and ethylenediamine (EDA) as capping agent. Thus obtained nanostructures display nanowire like networks with interesting inter-particle junctions that could help to enhance the Raman signal of analyte molecule.

## 2. Experimental

### 2.1. Materials

NaOH,  $\text{Cu}(\text{NO}_3)_2$ , and ethylenediamine (EDA) were obtained from SRL, India and the formaldehyde solution (37% w/v in  $\text{H}_2\text{O}$ ) was obtained from Fischer Scientific. All the chemicals were used as received. Milli Q water ( $18.2 \text{ M}\Omega\text{-cm}$ ) was used for the synthesis.

### 2.2. Method

12 g of NaOH was accurately weighed into a 60 mL glass vial and dissolved in 20 mL of Milli Q water. 1.5 mL of 0.1 M Copper nitrate trihydrate was taken as the Cu precursor and added to the above NaOH solution. After mixing the contents in the glass vial, 0.1 mL of EDA and 1.9 mL of formaldehyde were added. The reaction mixture was mixed thoroughly and allowed to stand at  $60^\circ\text{C}$  in a hot air oven till the blue colored solution turns to brownish black. The solution was centrifuged at 8000 rpm, dried and sample was subjected to further characterization.

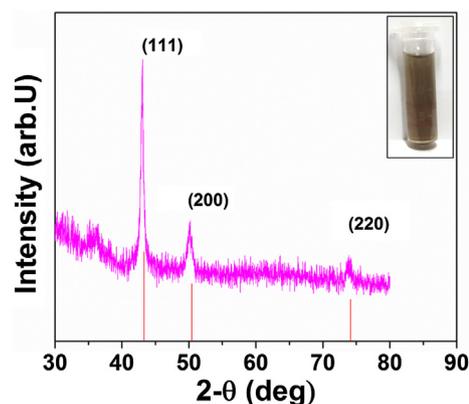


Fig. 1. PXRD of synthesized Cu nanowire like network structures. Photograph of the nanocolloid dispersed in *iso*-propyl alcohol (IPA) (Inset).

### 2.3. Characterization

PXRD of the synthesized sample was recorded on Panalytical X'pert powder (Netherland) using Cu  $\text{K}\alpha$  as X-ray source. HRTEM of the samples were recorded on FEI Technai S-Twin high resolution TEM operated at 200 kV. FE-SEM of the sample was recorded on SIGMA HV – Carl Zeiss with Bruker Quantax 200 – Z10 EDS Detector.

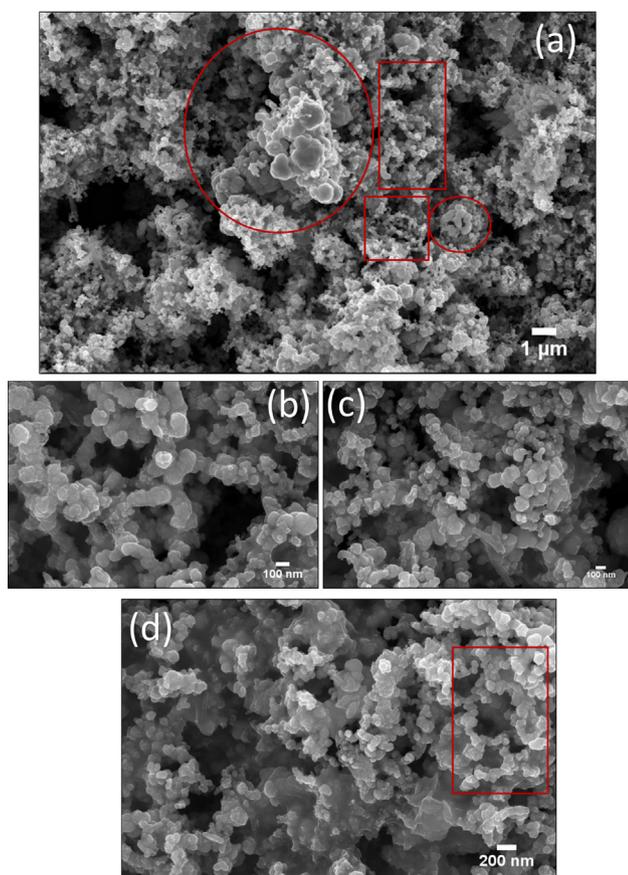
### 2.4. SERS measurements

Cu NPs were drop-casted on cleaned silicon (Si) substrates and dried at ambient conditions. Later,  $20 \mu\text{L}$  of  $5 \mu\text{M}$  Methylene Blue (MB) was dropped over the dried NPs film on Si. The Raman spectra were acquired with a portable Raman system (B&W Tek, USA) operated with a laser source at 785 nm, each spectrum was an average of 3 spectra at an integration time 5 s at 30 mW laser power.

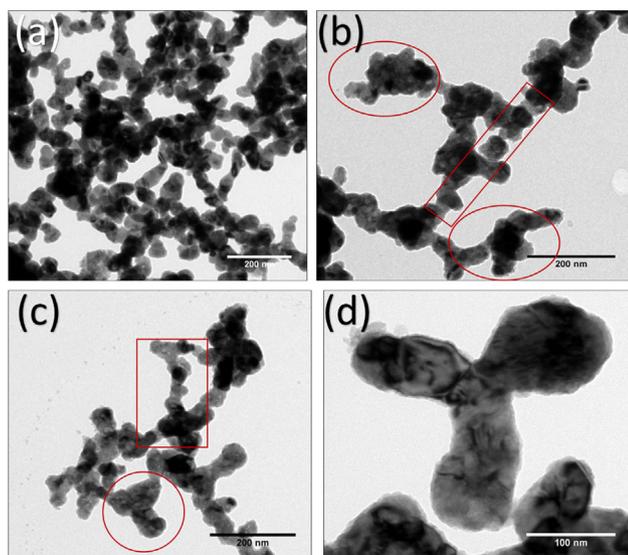
## 3. Results and discussion

Purified Cu nanostructures were characterized with PXRD (Fig. 1). The peak positions at  $\sim 43^\circ$ ,  $\sim 50^\circ$ ,  $\sim 73^\circ$  are assigned to (1 1 1), (2 0 0), (2 2 0) of FCC Cu respectively. Another low intensity peak at  $\sim 36^\circ$  represents (1 1 1) of  $\text{Cu}_2\text{O}$  which could be formed due to the surface oxidation of Cu. FE-SEM images of the Cu nanostructures are shown in the Fig. 2. Careful examination of the oval shape marked regions shows the aggregates of small particles and their incomplete ripening (Fig. 2a) and Cu nano-networks that are formed by the oriented attachment of Cu nanoparticles can also be observed in the rectangle shaped areas of SEM images (Fig. 2a and d). To understand this kind of aggregation and oriented attachment of Cu nanostructures, further we characterized the sample with TEM (Fig. 3). Careful observation of these images along the length of the nanowire like network reveals two types of interesting aggregation behavior *viz.* oriented attachment of individual nanoparticles in one dimension in which the fusion/merge of nanoparticles was incomplete (rectangular portions, Fig. 3) to form fully grown nanowires and aggregated nanoparticles with their incomplete ripening (oval portions in Fig. 3). To elucidate the origin of aggregation of nanostructures, it is important to understand the role of different reagents used in the synthesis of Cu nanostructures.

In our synthetic approach, EDA and formaldehyde are two important reagents that could produce Cu nanostructures with previously discussed morphological features. Since EDA is a well-established capping agent in the synthesis of Cu nanowires and nanoparticles, the another reagent formaldehyde alone could induce the reduction of Cu (II) to Cu(0). To validate this, we attempted to synthesize Cu nanostructures in the absence of formaldehyde that could not produce any Cu nanostructures (Supporting Information, Fig. S1). The earlier reports which describe the role of formaldehyde as reducing agent for the



**Fig. 2.** (a–d) SEM images of nanowire like networks and aggregations of Cu nanoparticles. Different type of aggregation either by (i) coalescence and Ostwald's ripening (ii) oriented attachment of the particles are indicated with oval and rectangular shapes respectively.



**Fig. 3.** (a–d) TEM images of nanowire like networks of Cu nanoparticles. Different types of aggregation either by (i) coalescence and Ostwald's ripening (ii) oriented attachment of the particles are indicated with oval and rectangular shapes respectively.

synthesis of other metal nanoparticles further support our observation [24,25]. Formaldehyde is known to be a slow reducing agent and its reducing ability can be enhanced by the addition of base catalysts [25]. Our experimental results also support this, as we did not observe the

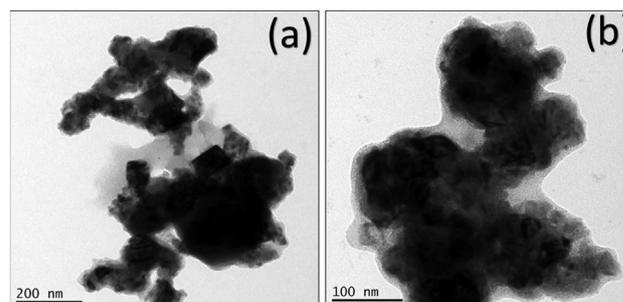
formation of Cu nanostructures when the synthesis was carried out in the absence of a base, under identical experimental conditions (Supporting Information, Fig. S2). Hence the synthesis of Cu nanostructures in basic medium can enhance the reducing power of formaldehyde besides forming a copper hydroxide complex, a necessary precursor complex for the synthesis of Cu nanostructures [26]. In the nanoparticles synthesis, formation of stable sol or powder depends on the nucleation-growth kinetics. In the presence of slow reducing agent like formaldehyde, nucleation kinetics are slow enough to induce the aggregation of nanoparticles [27]. However, random aggregation alone unlikely to happen as synthesis also involves the use of a capping agent *i.e.* EDA.

Capping agents are used in the synthesis of nanoparticles to passivate the nanoparticle surface and to minimize the surface energy of nanoparticles. If the synthesis of nanoparticles is carried out in the absence of capping agent, they tend to aggregate to minimize their surface energy. Besides, they also show aggregation (i) if the capping agent is inadequate (ii) if the capping agent is stripped off from the nanoparticle surface [28].

It is known that EDA promotes the growth of Cu nanowires in [1 1 0] direction by facilitating the addition of newly formed seed to {1 1 1} facets rather than {1 0 0} facets of Cu [29] which can lead to one dimensional growth of nanowires. As discussed earlier, if the concentration of the capping agent is not enough to cap the seeds adequately, then the addition of newly generated Cu seeds to both the facets *i.e.* {1 0 0} and {1 1 1} is feasible and generate other anisotropic structures [30] or rough nanowires [31]. Similarly, even in our approach, if the Cu seed is poorly capped with EDA, then newly formed Cu seeds are added to all the possible facets of inadequately capped Cu seed without any restriction. This is similar to coalescence of nanoparticles/ Ostwald's ripening and hence the structures in the oval marked portion can be observed (Figs. 2 and 3). On the other hand, when the seeds that are capped with adequate amount of EDA, addition of newly formed seeds to {1 0 0} facets was restricted. As a result, nanowire like network was observed which could be formed by the oriented attachment of nanoparticles (marked as rectangular portions, Figs. 2 and 3).

The above discussion on the aggregation of Cu nanostructures is mainly focused on the role of capping agent, *i.e.* EDA. Hence, to understand the role of EDA in the formation of Cu nanowire like networks, the synthesis of Cu nanostructures was performed under identical conditions in the absence of EDA (supporting information Fig. S3 for photograph and XRD of the Cu nanostructures). TEM images reveal the irregular aggregation of the particles synthesized in the absence of EDA (Fig. 4). Hence it can be confirmed that the EDA restricts the addition of particles to {1 0 0} facets and induces the formation of Cu nanowire like networks by oriented attachment. Nevertheless, we did not observe the formation of completely grown Cu nanowires that require further optimization of reaction parameters.

Electron diffraction pattern of the nanowire like network structures of Cu are shown in the Fig. 5. Second quadrant of the Fig. 5a shows the



**Fig. 4.** (a and b) TEM images of Cu nanostructures synthesized in the absence of EDA.

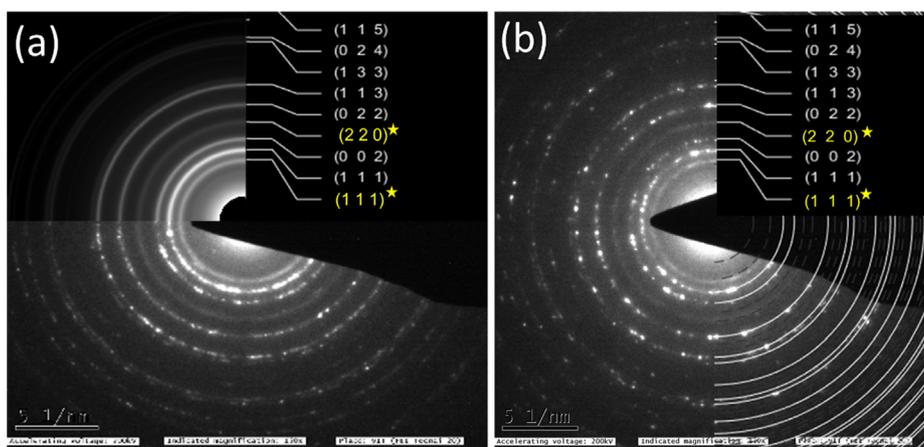


Fig. 5. (a and b) Representative electron diffraction of Cu nano networks and the ring patterns are indexed with corresponding planes of Cu. Ring patterns indexed with yellow corresponds to  $\text{Cu}_2\text{O}$ .

average intensity marked for clarity. 3&4 quadrants show the original ring pattern of the sample indicating the polycrystalline nature of the sample. In Fig. 5b, theoretical ring patterns are shown as continuous lines and forbidden patterns are indicated with dashed lines. Ring patterns are indexed and they are in good agreement with FCC of Cu. The presence of forbidden planes might be from the (1 1 1), (2 2 0) planes of  $\text{Cu}_2\text{O}$  that could be formed by the surface oxidation of Cu at ambient conditions. This was further supported by low intensity copper oxide peaks observed in the slow scan XRD of the sample (Supporting information, Fig. S4).

In the process of formation of network like nanostructures, we observed interesting inter-particle junctions as shown in the Fig. 6. These inter particle junctions form so called “hot spots” at which electromagnetic enhancement can occur [32,33]. Hence, we evaluated these nanowire networks for the SERS using MB as analyte molecule. Fig. 7(a) shows the Raman spectrum of 0.1 M MB on Si substrate without Cu nanoparticles. After drop casting the MB on Cu nanoparticles coated Si substrate, the Raman signal was observed even with micro molar concentration of MB (5  $\mu\text{M}$  of MB) (Fig. 7b). The enhancement factor was calculated by using the following relation.

$$\text{EF} = (I_{\text{SERS}} \times C_{\text{R}}) / (I_{\text{R}} \times C_{\text{SERS}})$$

where  $I_{\text{SERS}}$  is the Raman signal intensity with NPs,  $I_{\text{R}}$  is the Raman intensity without NPs,  $C_{\text{SERS}}$  is the concentration of sample on NP substrates (low concentration), and  $C_{\text{R}}$  is the concentration (0.1 M) of sample on bare Si, which produces the Raman signal ( $I_{\text{R}}$ ). We observed an EF of  $1.1 \times 10^4$  for MB using the Cu nano network structures. These Cu nanowire networks are also able to produce SERS signals of other commonly used dyes such as CV and R6G at 50  $\mu\text{M}$  concentration (EFs are  $7.8 \times 10^2$  and  $6.4 \times 10^2$  for CV and R6G, respectively) (Fig. 8). Although good EFs were reported with R6G using Cu nanostructures as SERS substrates, majority of these substrates were either produced by

physical methods or SERS data was recorded at high concentrations of R6G. Using chemically synthesized Cu nanostructures as SERS substrates, we achieved good EF comparable to earlier reports [19]. However, further optimization of reaction parameters/methods are required to produce robust Cu nanostructures as SERS substrates with high EFs. Exploring such promising Cu SERS substrates might be a progressive step towards the single use, economically feasible SERS substrate for point of care diagnostics.

#### 4. Conclusions

In this article, we demonstrated a chemical method in which simple organic molecule, formaldehyde solution used as reducing agent and EDA used as a capping agent to prepare Cu nanostructures. In the process of minimizing the surface energy of Cu nanoparticles, they tend to aggregate by oriented attachment or coalescence. As a result, we obtained Cu nanowire like networks with inter-particle junctions. The “hot spots” formed by inter-particle junctions could enhance the Raman signal due to electromagnetic enhancement. Hence these structures were examined as SERS substrate using MB, CV and R6G as analyte molecules. Such nanostructures will be promising to develop low cost SERS substrates in single use, point of care diagnostics.

#### CRediT authorship contribution statement

**K. Athira:** Investigation, Visualization. **M. Ranjana:** Investigation, Visualization. **M.S.S. Bharathi:** Investigation, Visualization. **B. Narasimha Reddy:** Investigation, Writing - review & editing. **T.G. Sathesh Babu:** Resources. **S. Venugopal Rao:** Validation, Formal analysis, Resources, Writing - review & editing, Supervision. **Darbha V. Ravi Kumar:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - original draft, Writing - review & editing,

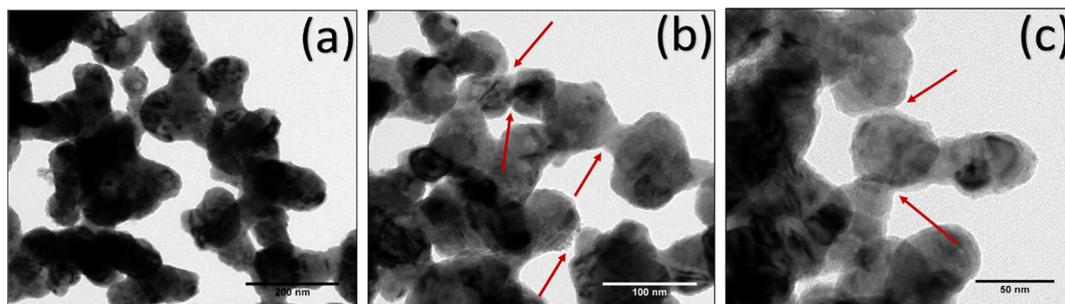


Fig. 6. TEM images of aggregates of Cu nanoparticles formed by oriented attachment of Cu nanoparticles. Junction between two particles may form hot spot that could increase the signal of Raman spectrum are indicated with arrow.

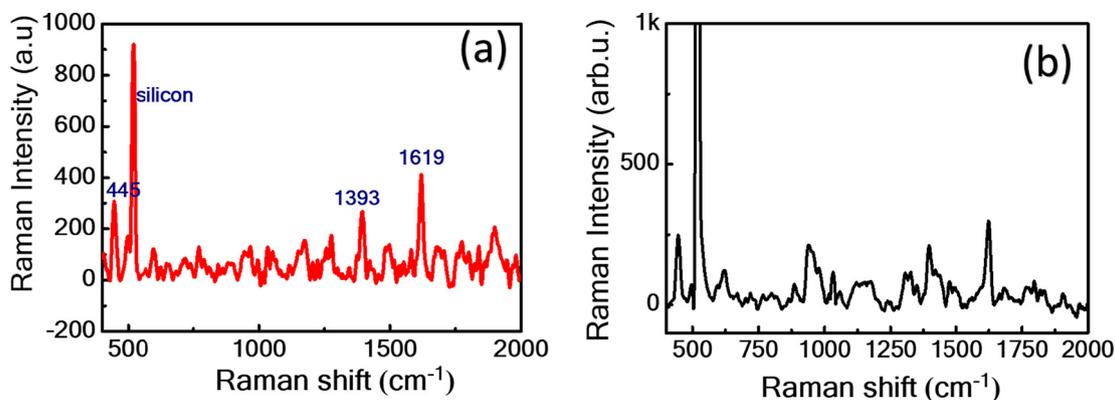


Fig. 7. Raman spectra of (a) 0.1 M methylene blue sample on Si substrate (b) 5  $\mu\text{M}$  of methylene blue on Cu nanocolloid.

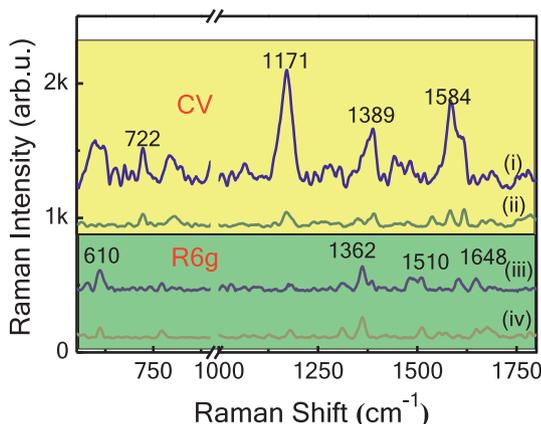


Fig. 8. SERS spectra (i) 50  $\mu\text{M}$  crystal violet (iii) 50  $\mu\text{M}$  R6G using Cu nanoparticles and normal Raman spectra of (ii) 5 mM crystal violet (iv) 28 mM R6G without Cu nanoparticles.

Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cpllett.2020.137390>.

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