Final report for project entitled "Nonlinear optical pulsed control of composite metamaterials", under Grant no. AOARD - 094042

The stated research goals of the project were:

We will investigate the properties of composite metamaterials where nonlinear materials are imbedded into the metamaterial structure. In particular we will look at development of theoretical schemes to optimize the nonlinear interaction between the probe and the pump (control) fields. A part of the strategy will also involve experimentally implementing some of these single layer composite metamaterials. The following issues will be specifically addressed:

1. Development of novel modalities to effectively achieve phase matching between the probe and the pump (control) radiation.
2. Study temporal pulse dynamics in order to optimize pump probe delays, intensities, carrier frequencies and the pulse bandwidths.
3. Incorporation of optical gain / amplification into the metamaterial structure in order to compensate for the inherent loss of the composite structure.
4. Fabrication of single layer composite metamaterial structures with imbedded resonant absorbers and undertake optical measurements of the transmission / reflectance properties.

Achievements in the project:

The main achievement in this project has been that we have been able to experimentally realize some of our theoretical ideas. The achievements can be classified into

1. Design of plasmonic metamaterial templates with large local field enhancements for the design of SERS templates.
    i. P. Mandal and S.A. Ramakrishna "*Dependence of surface enhanced Raman scattering on the plasmonic template periodicity",* Optics Letters **36**, 3705-3707 (2011)
    ii. P. Mandal and S.A. Ramakrishna, "S*urface enhanced Raman scattering from molecules on periodic gold and silver gratings made by Laser interference lithography", (In preparation, to be submitted to J. Opt. Soc. Am. B)*

2. Development of anodized alumina templates for the growth of long nanowires for the realization of anisotropic indefinite media – this work is being written up into a manuscript.

All the publication have / will have an acknowledgement to AOARD for the funding. In this report, we will outline the work carried out, highlighting the results and referring to the publication (attached with the report) for the detailed calculations.

One of the principal requirements for realizing our theoretical ideas in practice was the capability to make micro- and nanostructured materials. To this, under this project, we took up the fabrication of plasmonic patch metamaterials using laser interference lithography, nanosphere lithography and electro-deposition using anodized nanoporous alumina templates. The initial work started with the growth of plasmonic nanostructures using simple time and cost effective lithographic technique termed as 'Laser Interference Lithography'. Figure-1 below shows a flavor of the nanostructures fabricated in our laboratory: (a, b) obtained by laser interference lithography; (c) obtained by nanosphere lithography, (d) electron beam lithography (e) direct laser writing and porous alumina template method. We have now developed the capability to structure various kinds of materials over lengthscales from 100 nm to several micrometers over areas of few mm^2. Another requirement in developing controllable metamaterials is to be able to imbed nonlinear and gain materials within these micro- and nanostructures. We have taken the route of imbedding dye-doped

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14. ABSTRACT

Surface enhanced Raman scattering has been investigated from rhodamine 6G molecules embedded in polymethyl methacrylate (R6G ? PMMA) and coated on one-dimensional and two-dimensional gold-dielectric gratings fabricated by laser interference lithographically. The Raman signals from these plasmonic templates are 200 to 400 times larger than the signal from R6G ? PMMA coated on plain gold films. The enhancement of the Raman signal varies almost periodically with the period of the grating. Finite-difference time-domain simulations show that large electromagnetic near fields occur at the metallic edges due to the resonant excitation of localized surface plasmon of the gold patches by the pump laser. These give rise to large enhancements of the Raman signal. The dependence on period is due to the combined effects of the localized surface plasmon and the periodic grating that couples the pump laser to the surface plasmon polariton.

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polymeric materials using spin-coating methods. The problems of homogenous deposition, proper adhesion and compatibility of the materials have been addressed to a large extent.

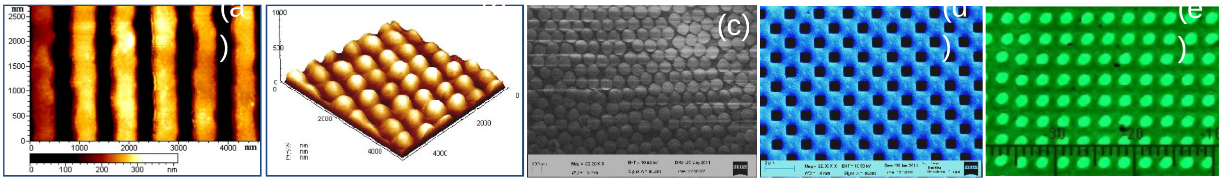


Figure-1. One-dimensional and two-dimensional structures (AFM images) fabricated in our group at IIT Kanpur by laser interference lithography (a, b), hexagonal array of silica particles (SEM image) grown by nanosphere lithography (c), square arrays of holes (SEM image) fabricated by electron beam lithography (d) and square arrays of circular holes (microscope image) obtained by direct laser writing (e). In (e) the scale bar is 0.8 m for the smallest division.

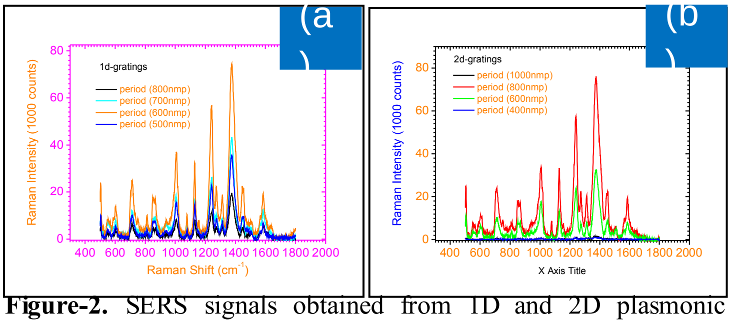
As a first step, the interest towards understanding the light-matter interaction by using controlled plasmonic nanostructures and metamaterials have led us to using the developed nano-plasmonic templates to investigate surface sensitive phenomena such as surface enhanced Raman scattering and surface enhanced fluorescence of active materials species as a function of various fabrication parameters. We used Rhodamine 6G doped polymers as a marker for the SERS. This is also in tune with our objective of imbedding dye-doped polymers in the metamaterials for gain and control. We observed very interesting experimental results which are discussed below. The findings have been supported by computer simulations and theoretical arguments.

1. Design of plasmonic metamaterial templates with large local field enhancements for the design of SERS templates

Using the templates fabricated by Laser Interference Lithography (LIL) we have thoroughly investigated Surface Enhanced Raman Scattering of active molecules such as rhodamine 6G (R6G) embedded in polymethyl methacrylate (PMMA). Surface Enhanced Raman Scattering has been a sensitive process for molecular level detection, molecular vibrational information and biological mapping [Baker *et al.*, Anal. Bioanal. Chem. Vol.-382, page-1751, year-2005]. It has been reported that Raman signal from molecules can be highly enhanced (order of 10^3 to 10^8) when placed on structured metallic objects due to strong electromagnetic near field localization around metallic objects. This strong localization of electromagnetic near–fields occurs at the metal edges, corners or regions between closely placed metallic nano objects termed as ‘hot-spots’. In the present investigation emphasis has been given to the controlling of such hot-spot regions by various controlling parameters as has already been mentioned above. Clearly, a reliable and reproducible Raman signal expected for the molecular species can only be feasible through such structured plasmonic templates. Similar potential applications have been found to surface enhanced fluorescence [Lacowicz *et al.*, Analyst, vol.-133, page-1308, year-2008], (presently under investigation).

We will now briefly describe the SERS results obtained from Raman active R6G+PMMA molecules placed on various plasmonic templates. Templates were fabricated through LIL using a 473 nm diode laser. After photoresist patterning by single or multiple exposures to the laser interference patterns and subsequent development, we deposited, by thermal evaporation, thin films of gold (Au) or silver (Ag) of 50 nm thickness on the patterned photoresist templates. Thus the deposited metals also have the pattern as that of photoresist. Finally Raman probe molecules R6G embedded in PMMA (solution) was spin coated onto patterned templates. The PMMA film with R6G molecules formed an approximate thickness of about 20 nm. The uniformity of the coating was checked using optical microscopy and found to be uniform. High dye concentrations of

millimolar orders were found to result in occasional micro-areas with dye agglomeration. But the dye concentrations used by us for SERS studies were of the order of 10 to 100 micromolar solutions. Raman spectra of R6G+PMMA on 1D as well as 2D patterned templates with different periodicities are shown in Figure-2. Laser diffraction spots observed from the templates consisted of highly discrete spots confirming the periodic patterning over a large area (~ 1 mm^2). In all the cases strong Raman peaks associated with various Raman transitions of probe molecules are observed.
All the samples show the same set of peaks and the peaks are associated with PMMA and R6G molecules [M. Michaels, M. Nirmal, and L. E. Brus, J. Am. Chem. Soc. 121, 9932 (1999); Matsushita, Y. Ren, K. Matsukawa, H. Inoue, Y. Minami, I. Noda, and Y. Ozaki, Vib. Spectrosc. 24, 171 (2000); X. Xingsheng, M. Hai, Z. Qijing, and Z. Yunsheng, J. Opt. A: Pure Appl. Opt. 4, 237 (2002)]. The largest Raman signal is obtained for the template with a periodicity of 600 nm and 800 nm for 1D and 2D cases, respectively. Relative enhancement factors calculated with respect to that of plain gold films and are seen to be in the range of 50 to 400 for the various transitions. Large Raman signal enhanced is due to concentrated electromagnetic near field near the metallic edges. FDTD simulations of the electromagnetic fields using a commercial Optiwave FDTD simulator on a model 1-D template typical for 600 nm period were performed to support experimental results. The simulated results are shown in figure-2 (c, d). We observed a very interesting modulation effect of enhanced Raman scattering on template periodicity. This modulation effect is found to be due to the combined effect of localized plasmon as well as propagating surface plasmon polariton resonance and the argument also supported through FDTD simulation (for details: **P. Mandal and S. Anantha Ramakrishna, Optics Letters, vol.-36, pages-3705-3707, year-2011**). Our findings have great potential for the design of plasmonic templates for SERS and similar plasmonic effects.



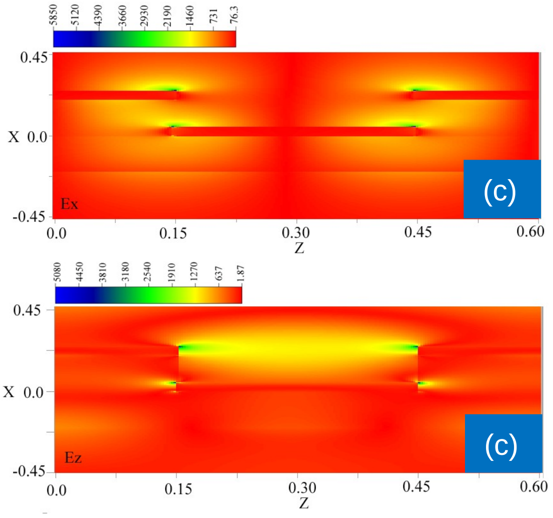


Figure-2. SERS signals obtained from 1D and 2D plasmonic templates (a, b, respectively) with changing periodicity. Probe molecular concentration in PMMA was 19 micro-molar. Gold was used as metal coating on structured photoresist for the plasmonic resonance. A typical simulation result of 1D grating (Ex and Ez field) for 600 nm period is shown in figure (c, d).

It is observed that the concentrated electromagnetic field mainly arises at the metal strip corner or edges or between two metal nano-objects. It is thus a general conclusion that the smaller and closer nano-objects with sharp edges will give rise to very large near fields, inferring that such structural configuration may be capable of single molecular detection by SERS. It is noted for the typical dye concentrations used by us (about 19 micromolar), it is estimated that each period of the plasmonic patch metamaterial surface contains only about 60 molecules. Given that the SERS pump laser spot was about 2 microns across in our experiments, we already are approaching the single molecule detection here. It is also important that the localized as well as propagating plasmon resonance will depend on the feature size and shape. Comparing the SERS enhancements to that obtained from molecules placed on evaporated plain gold films, we deduce that the field enhancements in our samples are of the order of 10^6.

Another aspect of the plasmonic excitation is the polarization of pump. While TM polarized light can excite SPP in 1D metallic objects the mesa-type or 2D grating will be helpful for both TM, TE, and mixed TM-TE excitations. Depending on the plasmonic resonance band and excitation wavelength or the coupling strength has strong impact on the over-all improvement of SERS or SEF signal. We will show below SERS data obtained for 2D templates (Ag is used as metal for plasmonic resonance source) with square as well as hexagonal lattice symmetries (Figure-3). For comparison data for 1D structure is also presented. The experimental observation is supported by 3D FDTD simulation. The experimentally observed SERS signal for 2D square geometry is larger compared to 1D case. It is also seen that the SERS signal is comparable for 2D square and hexagonal geometries. The large difference between in SERS signal for 1D and 2D cases arises due to stronger near field enhancement for the 2-D structures. This is confirmed from the simulated results as shown in figure (h-j). The detailed results for the 2-D structures are being written up as a manuscript for communication to J. Opt. Soc. Am. B.

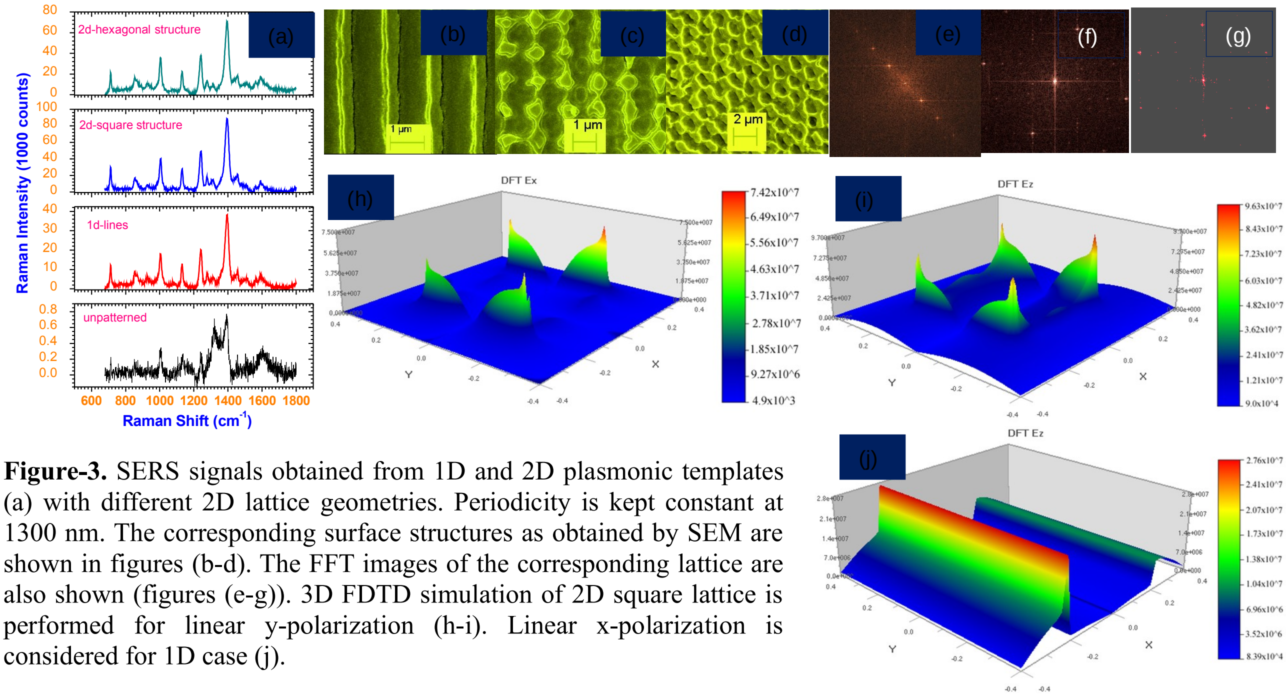


Figure-3. SERS signals obtained from 1D and 2D plasmonic templates (a) with different 2D lattice geometries. Periodicity is kept constant at 1300 nm. The corresponding surface structures as obtained by SEM are shown in figures (b-d). The FFT images of the corresponding lattice are also shown (figures (e-g)). 3D FDTD simulation of 2D square lattice is performed for linear y-polarization (h-i). Linear x-polarization is considered for 1D case (j).

Our study on the SERS enhancements from plasmonic patch materials confirms the presence of plasmonic resonances at 800 nm wavelength using various periodicities and sizes of the plasmonic patches. We are able to fabricate plasmonic patch templates down to 300 nm periodicity, which makes it possible to homogenize these into effective metasurfaces with imbedded nonlinearities for radiation of larger wavelengths of 1000nm and above.

2. Thin wire metamaterials: E-beam lithography and anodized nanoporous alumina templates for electrodeposition

Thin wire metamaterials represent an important class of metamaterials that are very versatile in their properties and reasonably simple to fabricate. Arrays of thin conducting wires with subwavelength periodicity show plasma like properties with a lowered plasma frequency that is determined by the period and metal fillinf fraction. The lowered plasma frequency arises due to a low filling fraction and large inductive effects [Pendry, AJ Holden, DJ Robbins, and WJ Stewart, J. Phys. Cond. Matt., **10**, 4785 (1998)]. Metamaterials, with wires running along all the three dimensions, have reasonably isotropic plasma-like behaviour. However, having thin metallic wires oriented only in one direction can render the system extremely unique: the plasma-like polarizability in one direction versus the positive dielectric permittivities in the other orthogonal directions render the permittivity tensor indeterminate [D. R. Smith and D. Schurig , Phys. Rev. Lett., 90, 77405 (2003)]. The dispersion of light in such media becomes hyperbolic and has many important implications. Chief among them is the hyperlens that makes possible sub-wavelength image resolution in the optical far-field [Z. Liu, H. Lee, Y. Xiong, C. Sun and X. Zhang, Science, Vol. 315, 1686, 2007]. Negative refraction in hyperbolic media has also been demonstrated.

We had proposed to make thin wire media for demonstrating controllable metamaterials at optical frequencies and decided to used two methods: e-beam lithography and electrodeposition using a anodixed nanoporous alumina (ANA) template. The former method gives very controlled features, but can also yield small structured areas and the wires will be parallel to the substrate. In the latter case, large the alumina template can be inexpensively prepared over large areas and can give rise to hexagonally ordered uniform pore arrays in the alumina and the metal can be electro-deposited into the pores. The wires will be vertically oriented to the substrate in the case, and this is a preferred orientation for anisotropic indefinite media and normal incidence of radiation. Since the metamaterial properties of thin wire arrays depend primarily on a volume filling factor and not on the relative placemenet of the wires to a first approximation, the periodicity of the wire arrays is not a primary issue rendering the fabrication by the alumina templates very relevant.

We have built elementary templates for metallization using both e-beam lithography and anodization methods. The scanning electron micrographs in both cases are shown below. The template preparation by e-beam lithography is yet to be properly optimized for slit sizes (which will be metallized) to about 50 nm. We are able to make long channels about 100 nm wide and with filling fractions form 10% to 50%. In case of the ANA templates, the anodization was carried out on high purity aluminum at about 18°C and resulted in very high aspect ratio nanopores of almost 60 nm diameters and 2 to 20 micron length. The nanopores are not completely uniform and and are not uniformly arranged due to the high temperature of anodization. One interesting observation was that the nanopores can be arranged in a linear fashion if the underlying aluminum sheet had microscratches. Most virgin aluminum sheets that are produced by rolling either have scratches or stress that cause such alignment of the pores in one direction. Upon electropolishing of the aluminum plate or removal of the formed alumina layer and subesquent second anodization, the linear alignment of the pores does not result. We have verified that such linear alignment can be reproduced by unidirectionally scratching the electropolished aluminum sheets. This result is presently being written up for publication and the paper will be communicated to AOARD as soon as it is prepared.

In conclusion, we have prepared the templates for fabricating the thin wire metamaterials for optical frequencies. We believe that with further work we will be able to prepare these metamaterials and also imbed within them controllable dielectrics for generating controllable metamaterials. This will be taken up in the subsequent years.

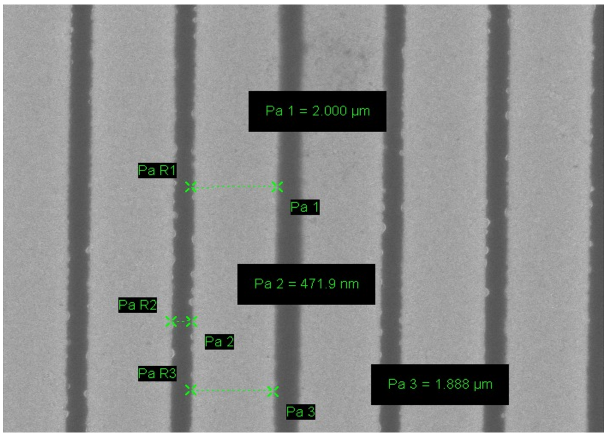


Figure 4a: SEM image of the nanolines (100 microns long) made by e-beam lithography. The dark areas are the unexposed PMMA which will be removed and metalized (work in progress). The filling fraction is about 25%.

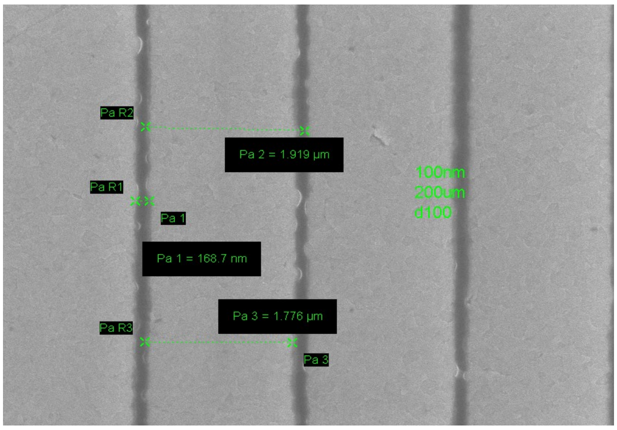


Figure 4b: SEM image of the nanolines (100 microns long) made by e-beam lithography. The dark areas are the unexposed PMMA which will be removed and metalized (work in progress). The filling fraction is about 8.5%.

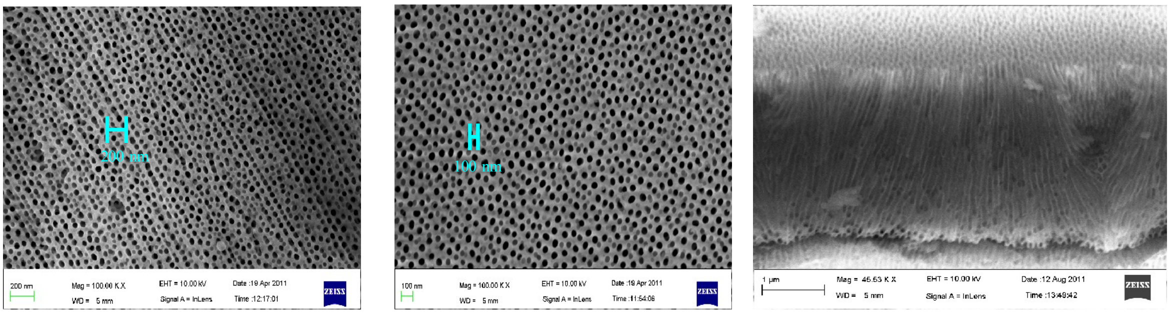


Figure 5: Scanning electron microscope pictures of anodized nanoporous alumina (ANA) surfaces with nanopores aligned on straight lines in (left) and tended to hexagonal order in (middle). The right panel shows a cross-section of the ANA that demosntrates the large aspect ratios of the structures. The typical pore sizes are about 60 nm.

Future aspects:

Plasmonic templates formed using laser interference lithography and anodized nanoporous alumina are good structures for SERS, SEF, sensors, nonlinear optical devices and optoelectronics. They can also provide gain for surface plasmon amplification and lasers (SPASER). The above mentioned topics are presently under investigation in our group.

Deviations from the original objectives with reasons

Due to our intense concentration on the development of the experimental setups and experiments, we could not work on the theoretical objectives (1) and (2). Further, in relation to Objective (1), we realized that only in very thick metamaterials, will the issue of phase matching be really important. From our previous experience of calculations of wave propagation in dissipative metamaterials, we realized that the system would be very dissipative rendering these questions of phase matching primarily of academic interest. We intend to take up the work under Objective (2) in the near-future and the AOARD will be duly acknowledged in publications on that work too.

Personnel involved with the Project:

1. Dr. Prasanta Mandal, Post-doctoral Fellow, Project Scientist (employed by this project)
2. Mr. Gangadhar Behera, Ph.D. Student, Physics department, IIT Kanpur
3. Mr. Dheeraj Pratap, Ph.D. Student, Physics department, IIT Kanpur
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