The large concentration of electromagnetic (EM) fields near metal nanoparticles upon illumination of light is one of the defining concepts of light matter interactions at the nanoscale. The strength of this so-called “near field” can be very large at the junction of two metal nanoparticles, which has facilitated promising technologies, such as the detection of single molecules through a large enhancement of the Raman scattering signal. The degree of enhancement of the near field increases rapidly as the particles are brought closer, thereby suggesting an atomically thin and uniform material, such as graphene, as the ideal spacer layer for maximum near field enhancement. Here we combine oblique angle deposition (OAD) technique with standard graphene transfer protocols to fabricate two metal nanoparticle arrays separated precisely by a small distance using the of previous graphene-based plasmonic devices, which signify the tremendous promise of this novel method of integrating plasmonics with graphene and other atomically thin materials.

When two nanoparticles made of noble metals under appropriate illumination are placed within few nm of each other, the EM field induced at their junction can get amplified by several orders of magnitude, thereby facilitating two technologies of immense current interest. These so-called “hot spots” have facilitated the detection of single molecules through surface enhanced Raman spectroscopy (SERS) which in turn inspired an entire field of research devoted to the development of substrates containing metallic structures with nanosized gaps in between. Beside SERS applications, the enhanced EM field at nanoparticle junctions can also be used to enhance the performance of various optoelectronic devices, such as those pertaining to photovoltaics and high-speed wavelength-selective photodetection.

In electrostatics, the electric field between two oppositely charged plates varies inversely as the distance between them, which arises due to Coulomb interactions between the charges residing on the two plates. Similarly, the dependence of the EM field enhancement on the size of the gap (d) originates in the EM interactions between the localized plasmon modes of two neighboring nanoparticles (radius a). In the simplest approximation, each particle can be approximated as an electric dipole whose strength is proportional to the net electric field at its location, where a is the polarizability of the particle at the wavelength of illumination. The contributions to the net electric field for particle 1 come from the incident field (E_0), as well as the electric field due to the dipole (p_i) of particle 2 at the location of particle 1, where the dominant term of E_j \propto \frac{1}{d^6}, thus implying a strong distance dependence of the dipolar coupling. This approximation breaks down for d < a, beyond which higher order multipolar contributions needs to be taken into account, where numerical calculations can provide an accurate picture. Also important is the direction of propagation and state of polarization of the incident beam, and their relation to the interparticle axis. As an example, let us consider a metallic nanosphere illuminated by a plane wave with a wavelength of 530 nm. The electric field due to this illumination can be approximated as a dipole moment p_i a, where a is the radius of the sphere. The electric field at the location of another nanosphere of radius a is given by E_j \propto \frac{p_i a}{d^6}, where d is the distance between the two spheres. This expression is known as the Rytov approximation, and it shows that the electric field at the location of the second sphere is proportional to the electric field at the location of the first sphere, multiplied by a factor that depends on the distance between the two spheres. The Rytov approximation is valid for distances greater than the radius of the sphere, but it breaks down for distances less than the radius of the sphere. In this case, a more accurate calculation is required to determine the electric field at the location of the second sphere.
The distance dependence of \( \left( \frac{|E|}{|E_0|} \right)^2 \) max for three illumination wavelengths is shown in Figure 1c.

The engineering challenges to develop such a system are primarily related to the smallest gap that can be reliably and reproducibly obtained with the chosen method of fabrication, with a possible emphasis towards the development of large area substrates using scalable techniques. Commonly used systems, such as aggregates of metal colloids, suffer from the randomness of the gap size and therefore the EM field enhancement, whereas the typical resolution [11] achievable with electron beam lithography being greater than 5 nm, renders standard lithographic approaches mostly ineffective. Among various wafer scale methods, the array of metallic nanopyramids obtained with nanosphere lithography [12] is common, although it suffers from the nonuniformity of the gap sizes below few nm. This is also true for recently reported [13] self-assembled pair of gold nanorods whose separations varied between 0.5 and 2 nm. Alternate approaches towards fabricating uniform and reproducible nm sized gaps have relied on using a thin spacer material, such as polyelectrolyte [14] coating (thickness > 3 nm) or SLG [15] (spacing 0.34 nm) separating a collection of gold colloids from a thin film, also made of gold. One shortcoming of this method is related to the conductivity of the underlying metal film, which makes this method incompatible with applications aiming towards improving the photodetection efficiency of the thin spacer material. The solution that presents itself is therefore not to use a gold film, but rather place a spacer material between a pair [16–18] of metal nanoparticles. For realistic applications requiring large area devices, an attractive possibility would be to use two arrays of plasmonic nanoparticles separated by a suitable spacer material, which by virtue of its large near field focusing, can be used as a sensitive SERS substrate, and as a photoresponsive device as well. As we demonstrate in this paper, an almost ideal solution can be achieved with a SLG acting as a spacer between two arrays of silver nanoparticles, giving rise to extremely large and localized EM fields, resulting in a 100-fold enhancement of the SLG photoresponse.

Three properties of graphene make it an ideal candidate as a spacer material: (i) graphene can be used as a standard for Raman [19–22] measurements, since its Raman scattering is highly reproducible and well understood. Additionally, it is possible to functionalize graphene with various chemicals, which in conjunction with the highly enhanced near field, allows graphene to be an ideal substrate for SERS measurements. (ii) In spite of its low absorption, graphene shows broadband and fast photoresponse, and therefore promising as a material for photodetection. (iii) Most importantly, it is one of the thinnest materials available, with thickness precisely that of an atom (0.34 nm), thereby allowing a very large enhancement of the EM field at the junction of the nanoparticles, as shown in Figure 1c. An important question that arises is whether this is the highest field enhancement one could achieve, or...
whether further reduction in the gap can result in even larger \((|E_1|/|E_0|)^2\). For the estimates shown in Figure 1, the nanoplasmonic system was assumed to follow classical electrodynamics in Drude local response approximation. For such tiny gaps, there could be significant contribution from nonlocal\(^{[28-30]}\) response of the dimers, which could result in lower EM field enhancement with respect to the estimates obtained from local response approximation. Besides, for separations around 0.3–0.5 nm, quantum tunneling\(^{[28-30]}\) of plasmons are predicted to limit the maximum enhancement of the optical fields at the junction, although similar effects have also been predicted by recent\(^{[31]}\) semiclassical treatment of the nonlocal response. Taken together, single layer graphene appears as a near ideal spacer material for plasmonic dimers.

Achieving the proposed device architecture of a pair of 2D arrays of metal nanoparticles separated by SLG required the confluence of multiple fabrication schemes. While multiple protocols exist for large area assembly of colloidal particles and subsequent deposition of SLG, placing a nanoparticle array directly above another is not trivial.\(^{[32]}\) In this work, this was achieved by OAD\(^{[33]}\) of a metal film with active substrate cooling,\(^{[34]}\) and subsequent annealing, a method that can be broadly classified as a type of directed self assembly. We chose the spacing between adjacent nanoparticles within an array to be quite large, similar to the wavelength of illumination used in the experiments reported here. Accordingly, we could neglect the plasmon interactions between neighboring dimers within the array, consistent with the assumptions made in the theoretical calculations shown in Figure 1b,c. The large interparticle separation also allowed us to image the large near field concentration at the colloidal junctions using Raman spectroscopy. The sequence of steps used for fabricating the metal arrays separated by graphene is shown in Figure 2. The initial pre patterning of the Silicon wafer was achieved by depositing a monolayer of silica beads of radius 250 nm with standard lift off method. A subsequent electron beam evaporation of silver at an extreme angle to the wafer ensured the formation of metal islands at the top of the beads, which became spherical (of radius \(70\) nm) following a simple heating step. This resulted in the formation of a triangular array of metal nanoparticles of spacing 500 nm defined by the underlying array of silica beads, after which we used standard protocols to transfer a layer of chemical vapor deposition (CVD) grown graphene on the top of the array. This was followed by a similar procedure of depositing silver at an extreme angle and annealing it subsequently. The extreme angle of evaporation ensured the second layer of silver to be placed directly above the annealed silver nanosphere, separated by SLG. The substrate was cooled to liquid nitrogen temperatures during both the evaporation steps, such as to minimize the diffusion of the silver atoms. As seen from the scanning electron microscopy (SEM) images, i) the graphene layer remained well connected even after the entire fabrication process, implying its suitability for electrical transport measurements, although small amount of wear-and-tear in the SLG could also be seen and ii) the near spherical structure of the nanoparticle due to minimal wetting of graphene by silver during the deposition and/or annealing process. The imperfections were primarily caused by the defects in the arrangement of the underlying array of silica beads, although the quality of SLG grown by the CVD growth and structural damage during the transfer process was also important. It is important to note that the methods used in our fabrication were completely scalable, implying it will be possible to extend this process flow to wafer scale devices in future.

To make a quantitative estimate of the enhancement of the EM field, we measured the Raman scattering spectrum under normal incidence arising from the SLG sandwiched between the two arrays of silver nanoparticles. The strength of the Raman signals of the sandwiched SLG was much larger compared to bare SLG (without silver nanoparticles), as shown in the typical spectra shown in Figure 3a. The increase in width of the characteristic Raman bands for the sandwiched structure is related to the strains developed in graphene due to its (partially) suspended configuration, in agreement with studies reported\(^{[35]}\) before. We took the ratio of the total area \((A_C\) or \(A_{2D}\)) under each Raman band as an appropriate measure of the strength of the Raman signal. Accordingly, the ratio of the \(A_C\) (or \(A_{2D}\)) of the sandwiched structure to that of bare graphene provided an estimate of the plasmonic enhancement of the Raman

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**Figure 2.** Method of fabrication. Schematic of the fabrication steps along with representative SEM images: i) OAD of silver on a monolayer of silica beads with the substrate at 80 K; ii) annealing the substrate to render the silver particles spherical; iii) transfer of SLG (SEM image shown); iv) second OAD of silver while keeping the substrate at 80 K; and (v) annealing the substrate to render the silver islands spherical (SEM image shown).

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signal, which was expected to be highest at the junction of the silver colloids, positioned directly above individual silica beads arranged in a hexagonal geometry. As shown in Figure 3c, a pattern with approximate periodicity 500 nm could be detected, implying the maximum Raman signal was probably arising at the nanoparticle junctions as per design. A histogram of the Raman enhancement for 2D (top) and G (bottom) bands, where we consider the area, arrows indicate the positions of the numerical estimate. Figure 3d) Variation of \(\left(\frac{|E_p|}{|E_{pol}|}\right)^2_{max}\) with wavelength \(\lambda\). The wavelengths corresponding to the excitation laser (532 nm) and the emission (G – 580 nm and 2D – 621 nm) have been marked with arrows. (Inset) Showing the square of the parallel components of the enhanced EM fields, given by \(\left(\frac{|E_p|}{|E_{pol}|}\right)^2\), for illumination wavelength 530 nm, showing the strong confinement of the EM fields within a small region of area, \(\sigma_p = 12 \text{ nm}^2\). See the Supporting Information for details of estimation of \(\sigma_p\). All dimensions are in nm.

To verify that the observed increase in the Raman signal was indeed due to plasmonic enhancement, we estimate the strength of the EM field localized in each hot spot. We consider the distribution of the Raman signal enhancements for two Raman bands (2D and G), shown in Figure 3c. The enhancement was larger in the G band (20 ± 7.6) compared to 2D (3 ± 1.36), which could be understood by considering the mechanisms leading to the enhancement of the Raman signal. The primary source of the enhancement was due to the component of the strongly enhanced near field parallel \(E_p\) to the SLG, amounting to \(\left(\frac{|E_p|}{|E_{pol}|}\right)^2_{abs} = 7543\) at the wavelength of the excitation laser (532 nm), as can be seen from the numerical simulations shown in Figure 3d. Note the largely enhanced EM fields were concentrated in a very small region of area \(\sigma_p = 12 \text{ nm}^2\) at the junction of the particles, as shown in Figure 3d. The secondary source of enhancement was due to the local electric enhancement at the Stokes-shifted emission wavelengths, which corresponded to \(\left(\frac{|E_p|}{|E_{pol}|}\right)^2_{emi} = 125\) (580 nm) and 21 (620 nm) for the G and the 2D bands, respectively. The net enhancement of the Raman signal for the laser focal spot of area \(A = 0.4 \mu \text{m}^2\) was therefore given by \(\left(\frac{|E_p|}{|E_{pol}|}\right)^2_{abs}\left(\frac{|E_p|}{|E_{pol}|}\right)^2_{emi}\left(\sigma_p/A\right)\), which amounted to be around 28 and 5 for the G and 2D bands, respectively. These values were reasonably close with the experimentally measured enhancements (20 ± 7.6 and 3 ± 1.36, respectively). Although the agreement was well, the large variability in the Raman signal (see the wide histograms shown in Figure 3c) merits some discussion. We believe this was due to the nonexact placement of the particles along the \(z\)-direction, something that was related to the spot to spot variability of the wafer scale fabrication scheme. This formed a source of experimental variability but could not be incorporated in the numerical model in any simple manner. The numerical model also neglected the non-local effects, which could change the results to some extent. Accordingly the quantitative agreement between the numerical and experimental Raman signals should be considered as approximate.

While the Raman enhancement can be exploited in molecular sensing (using SERS) by functionalizing the sandwiched
graphene, the double-layer structure also allows, as we demonstrate below, a new class of graphene–plasmonic photodetector with unprecedented sensitivity. Although several protocols ranging from nanostructuring \cite{37} to hybridizing graphene with other semiconductors \cite{38-41} are now available to overcome the intrinsically weak light response of the bare graphene photodetectors \cite{42,43}, sensitizing graphene by coupling to plasmonic \cite{44,45} structures offer the unique advantage of enhanced photoresponse without sacrificing the detection bandwidth. Recent experiments with lithographically \cite{46} and thermally treated \cite{47} metallic nanostructures imprinted onto exfoliated or CVD-grown graphene revealed over ten times increase in photoresponsivity in comparison to that of bare graphene at the resonant wavelengths. However the graphene channels in such devices were supported by insulating substrates and plasmonic enhancement was restricted only to the exposed side of graphene unlike the double-layer plasmonic focusing in the present case of graphene sandwiched between the nanoparticle dimers.

In order to evaluate the photoresponse of the graphene–silver dimer assembly titanium (Ti)–gold (Au) source and drain electrical contacts were shadow evaporated onto the assembly placed on insulting SiO₂ substrate (schematic in \textbf{Figure 4a}).

As the micrograph in the inset of \textbf{Figure 4a} shows, our devices were macroscopically large (typical length \( \approx 0.4 \) mm and width \( \approx 0.8 \) mm), where the entire device area was illuminated (global illumination) with light emitting diodes (LEDs) of three different wavelengths centered around 470 nm (blue), 535 nm (green), and 635 nm (red). The source–drain current \( (I_{ds}) \)–voltage \( (V_{ds}) \) characteristics of the device under both dark and illuminated conditions were both found to be linear with a nominal two-probe resistance of \( \approx 5.7 \) kΩ (inset of \textbf{Figure 4b}).

\textbf{Figure 4b} shows the photoresponse of the graphene–silver dimer hybrid for all three wavelengths recorded at 180 K at the same LED power level \( P_{LED} \approx 0.51 \) µW mm\(^{-2}\) (see the Supporting Information for experimental details). Within the experimental range of \( |V_{ds}| \leq 2 \) V, the photocurrent \( I_p = I_{light} - I_{dark} \), where \( I_{light} \) and \( I_{dark} \) are the measured source–drain currents in illuminated and dark conditions, respectively, varies linearly with \( V_{ds} \) irrespective of illumination wavelength. Maximum photocurrent as large as 400 nA was obtained for the blue illumination, which is about a factor of ten greater than that for red light emphasizing a strong wavelength selectivity. Our measurements with control devices of identical geometry where bare CVD graphene was laid directly onto the SiO₂ substrate yielded much weaker (<10 nA) photocurrent when subjected to similar...
excitations, implying that the large photoresponse to be directly associated with the presence of nanoparticle dimers.

While strong color-selectivity readily suggests the enhancement in the photodetector response to be due to plasmonic coupling of the EM radiation to graphene via the nanoparticle dimers, we discuss the possible mechanism of photosensitivity in our devices, which commonly arises from photovoltaic, photo-thermoelectric or bolometric processes.\(^4\) A significant electron–hole asymmetry is unexpected in our simplistic two-probe device structure, where the entire layer of graphene is suspended on the array of metallic nanoparticles. This eliminates a significant contribution from the photothermoelectric effect.\(^2\) Second, a photovoltaic effect due to the band bending (over a length scale of \(\approx 200 \text{ nm}\)) at the contacts,\(^2\) as illustrated in the schematic of Figure 4a, arising from the work function difference at the contacts can lead to separation of the photogenerated electron–hole pairs.\(^2,5\) In our devices, the contact-induced doping can be marginally asymmetric (Fermi energy \(\Delta \text{eV} = 0.1 \text{eV}\)) due to slight shift of the Ti (mild electron doping) deposition with respect to Au (hole doping) during the shadow evaporation process (micrograph in Figure 4a). However, we found \(I_p\) to be zero at \(V_{gs} = 0\) within experimental accuracy in all measurements (Figure 4b), confirming that the photogenerated carriers are generated and separated in the bulk of the graphene rather than at the contacts. This is indeed expected for nanoparticle dimer-mediated photodetectors, because the large inter-dimer separation (\(\approx 500 \text{nm}\)) in comparison to the spatial scale of band bending at the contacts makes EM field enhancement in contact region far less likely.

In electrically biased graphene photodetectors, both photovoltaic and bolometric processes can lead to photocurrent generation in the bulk. Since the graphene in our device is un gated and naturally suspended, it exists close to the Dirac point where the photovoltaic effect via generation of nonequilibrium carriers is expected to dominate. This leads to photocurrent generation in the direction of the biasing current (positive photosponse), as indeed observed in our experiment (Figure 4b). Assuming the photocurrent depends on the density \(n_c^o\) of the nonequilibrium carriers as \(I_p = \frac{W L}{e V_{gs}} n_c^o\),\(^2\) the experimentally observed \(I_p \approx 0.2 \mu A\) at \(V_{gs} = 1 \text{ V}\) and illumination power \(P_{\text{LED}} = 0.25 \mu W \text{ mm}^{-2}\) can be obtained with net external quantum efficiency of \(\approx 1\%\), which is reasonable considering the highly disordered nature of the CVD graphene used in our experiments (carrier mobility \(\mu = 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)). In fact, the temperature coefficient of conductivity in our devices is positive even at room temperature (see the Supporting Information), which can be attributed to charging of the traps by photogenerated carriers which degrades photosensitivity dynamically. The charged traps increase the resistivity of the graphene channel thereby reducing the source drain current and hence act oppositely to the overall positive photosresponse due to plasmonic focusing. We emphasize this limiting influence of the charge traps in our case irrespective of the wavelength of photoexcitation, which is in contrast to the graphene–semiconductor nanoparticle hybrids where the nanoparticles assist in enhancing the photoconductivity by separating the photoexcited electrons and holes.\(^1\) Nonetheless, it is remarkable that in spite of the deteriorating impact of the traps we could obtain such high photosensorivity, suggesting a great scope of improvement in the performance of these graphene/dimer assemblies by carefully optimizing the growth and transfer process. To investigate whether the strong EM field focusing by the metal dimer array is ultimately responsible for the enhanced photosresponse in our devices we numerically estimate the expected enhancement factor of the effective responsivity. Considering that experimentally observed \(\gamma\) depends on two factors: first, band bending caused by \(V_{ds}\), and second, spatially averaged enhancement of the effective EM intensity, we can write,

\[ \gamma(\lambda, V_{ds}) = \gamma_0(V_{ds}) \times \left( \frac{1}{A_\text{det}} \int \int dxdy \left( \frac{E_x}{E_{\text{cell}}} \right)^2 \right) \]
where $\gamma$ ($V_{th}$) is the responsivity of a bare graphene photodetector at the same level of band bending. The second factor on the right hand side of the above equation can be computed from the near field EM intensity enhancement (Figure 1c) and shown as the solid line in Figure 4c for a triangular lattice of dimers with mean distance of $\sim$500 nm ($A_{cell}$ represents the area of a unit cell). We find a satisfactory agreement between the computed enhancement factor when the observed $\gamma$ for each color shown in Figure 4c is scaled by $\gamma_0 \approx 20$ mA W$^{-1}$, which is typical for electrically biased graphene photodetectors and also close to the photoresponsivity estimated for our control devices of similar geometry. While the agreement should be considered qualitative, it indeed provides a strong support to the nanoparticle dimer-mediated plasmonic enhancement of photoresponse in graphene.

In conclusion, we have demonstrated a conceptually novel method to integrate plasmonic nanoparticles with graphene, such as to achieve unprecedented EM field enhancement and photodetection sensitivity. The scalability of the entire process flow allow the development of large area devices, while the fabrication technique is general enough to be easily applicable to plasmonic nanoparticles of other sizes and materials (e.g., Gold, Aluminium, etc.), arrays of other 2D geometries, as well as other atomically thin spacers (e.g., MoS$_2$). This in turn may allow spectral tunability, necessary for both SERS and optoelectronic device applications, while engineering the coupling of plasmonic arrays at precise nm level separations could lead to photonic metamaterials with novel functionalities.

Experimental Section

**Numerical Simulations**: We used a commercial finite element based tool (COMSOL Inc.) for our numerical simulations. The 3D model geometry contained two silver nanoparticles (radius 70 nm) separated by 0.34 nm, surrounded by perfectly matched layer (PML) of thickness $\lambda/2$, was placed 2.54 distance away the dimer. A dynamic tetrahedral meshing of $\sim$900 K mesh elements of maximum mesh element size of 4.5 nm and $\lambda/6$, and minimum mesh element sizes of 0.12 nm were chosen. The convergence of the code was checked by varying the fault tolerances. We also validated the numerical results against similar calculations reported in the literature.

**Fabrication Details**: We cleaned a Si wafer (with top SiO$_2$ thickness of 285 nm) with acetone and isopropyl alcohol (IPA) and formed a mono layer of silica beads by the standard lift off method. The technique is based on our previous report on the assembly of metallic islands on dielectric structures using OAD (oblique island deposition) in a commercial electron beam evaporator, where the normal to the substrate was at angle of 84° to the direction of incoming vapor. We have cooled the substrate to liquid nitrogen temperatures for minimizing the diffusion of the metal atoms, and subsequently annealed at 350 °C for about 25 min in Argon atmosphere, such as to obtain nearly uniform spheres. A single layer of CVD graphene was transferred on the substrate, following which a second layer of Ag was deposited by the same method (cooled OAD). The substrate is subsequently annealed at 200 °C for about 10 min to make the top layer of Ag particles spherical, thereby forming a dimer structure separated by SLG. SEM images taken in a time gap of few months were very similar, implying the device to be completely stable over time.

**Raman Measurements**: The Raman measurement was done using a “Horiba Jobin Yvon LabRAM HR Raman” instrument with the excitation wavelength at 532 nm using a 100X objective of numerical aperture (NA) = 0.9. The Raman map was done at a scan step increment of 300 nm with a laser power of approximately about 1.45 mW and an integration time of 3 s.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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