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Templated electrokinetic directed chemical assembly for the fabrication of close-packed plasmonic metamolecules

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1. ABSTRACT

Colloidal self-assembly combined with templated surfaces holds the promise of fabricating large area devices in a low cost facile manner. This directed assembly approach improves the complexity of assemblies that can be achieved with self-assembly while maintaining advantages of molecular scale control. In this work, electrokinetic driving forces, i.e., electrohydrodynamic flow, are paired with chemical crosslinking between colloidal particles to form close-packed plasmonic metamolecules. This method addresses challenges of obtaining uniformity in nanostructure geometry and nanometer scale gap spacings in structures. Electrohydrodynamic flows yield robust driving forces between the template and nanoparticles as well as between nanoparticles on the surface promoting the assembly of close-packed metamolecules. Here, electron beam lithography defined Au pillars are used as seed structures that generate electrohydrodynamic flows. Chemical crosslinking between Au surfaces enables molecular control over gap spacings between nanoparticles and Au pillars. An as-fabricated structure is analyzed via full wave electromagnetic simulations and shown to produce large magnetic field enhancements on the order of 3.5 at optical frequencies. This novel method for directed self-assembly demonstrates the synergy between colloidal driving forces and chemical crosslinking for the fabrication of plasmonic metamolecules with unique electromagnetic properties.

2. INTRODUCTION

Metal architectures using colloidal nanoparticles as meta-molecule building blocks have shown great promise as a scalable self-assembly method to control light matter interactions in large area devices. The magnetic interaction of light and matter at optical frequencies is negligible compared to its electric counterpart[1–4] as natural magnetism fades away at infrared and optical frequencies. By forming discrete sub-wavelength clusters, devices that rely on narrow-band resonances — i.e., Fano resonances — based on dark (i.e., low scattering) electric and magnetic resonances can be realized.[5,6] Conventional split-ring resonators, that in principle could provide narrow band resonances, are prohibitively difficult to scale down to optical wavelengths,[7] whereas coupled nanospheres can be scaled.[8] As these architectures are composed of subwavelength building blocks, traditional optical lithography methods cannot be utilized for large area device fabrication. Optical magnetic resonators composed of nanoparticle building blocks have shown that large magnetic dipoles, and suppression of electric dipoles are achievable.[9,10] These systems lead to highly confined, extremely large magnetic fields which are designed to probe magnetic transitions in molecules at optical frequencies.[11] Optical frequency magnetic resonator structures are of special interest for templated self-assembly (directed assembly) because they can be composed of close-packed nanoparticles.[12] Still, control of gap spacings and particle geometries within metamolecules is an ongoing challenge in directed assembly.

In this work, in order to assemble plasmonic metamolecules, chemical crosslinking, using carbodiimide based chemistry, between nanoparticles and templates is selectively performed on surface using electrohydrodynamic (EHD) flow as a driving force. Templates are composed of Au pillars on the substrate's surface. These pillars serve as perturbations that drive EHD flow and electrophoresis, directing the assembly of

nanoparticles around the pillars. Induced by an electric field in colloidal solution, EHD flow promotes lateral motion and close-packing of particles in colloid at an electrode surface, thereby, assembling transient close-packed structures.[13,14] We freeze in transient structures with local carbodiimide[15–17] crosslinking. The EHD flow increases the nanoparticle residence time at small interparticle spacings; this is necessary to enable the O-acylisourea – lipoic acid pathway of the carbodiimide crosslinking to occur in high yields. This chemical pathway leads to an anhydride bridge between ligands on Au nanoparticles, yielding permanent close-packed nanoparticle oligomers.[18] The metamolecules produced with this technique are simulated and shown to deliver large magnetic resonances at optical frequencies. This work represents a step forward for directed assembly of nanoarchitectures to create metasurfaces by demonstrating the influence of both the template and physical driving forces in assembly to control oligomer morphology and uniformity of gap spacing. Close-packed plasmonic metamolecules fabricated using the EHD – anhydride assembly method have already been demonstrated as effective biosensors using their electric field enhancements,[19] now we pave the way forward to their use in sensing magnetic transitions in biomolecules.
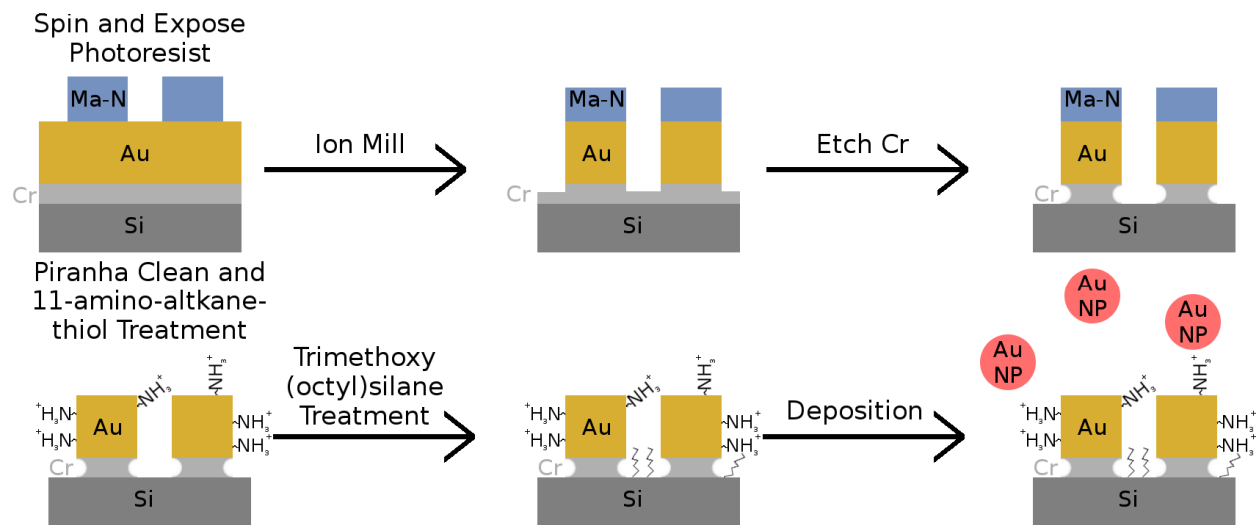
3. METHODS

Figure 1: Schematic of the fabrication process for seeded growth of close-packed metamolecules

3.1 Chemically functionalized Template Fabrication

Arrays of Au nanopillars on silicon are prepared using electron beam lithography (EBL), depicted in Figure 1. First, a highly doped Si wafer (0.004 ohm-cm) is cleaned via a standard cleaning protocol: 1) Piranha acid treatment for 15 minutes 2) Sonication in Acetone for 5 minutes 3) Sonication in IPA for 5 minutes 4) Nitrogen drying 5) Vacuum baking at 200 ^{0}C for 5 minutes. 45 nm of Au with a 5 nm Cr adhesion layer is electron-beam evaporated (Angstrom) onto the clean Si wafer. The Au on Si wafer is diced and cleaned again. Ma-N 2400 negative tone photoresist (Microchem) is spin-coated onto the clean Au on Si substrates and baked at 90^{0}C for 1 minute. Pillars are defined by exposing the photoresist with an electron beam (FEI) and a 1 minute development in Ma-D 525 (Microchem). The Ma-N pillars are used as a mask for ion milling (IntIvac), where the samples are etched until reaching the Cr layer, leaving Ma-N on Au pillars. The Cr layer is etched with Cr etchant (Sigma Aldrich) to avoid any overetching of the pillars with ion milling. The Ma-N is removed via piranha cleaning and samples are rinsed with deionized water and dried with nitrogen. Next two self-assembled monolayers are formed on the substrate. The Au pillars are selectively functionalized with Amine terminated ligands by overnight treatment of 0.5 mMol 11-Amino-alkane-thiol (Sigma Aldrich) in ethanol overnight. Samples are vigorously rinsed in methanol and dried with nitrogen. The Si wafer is then selectively functionalized via a vapor phase with trimethoxy(octyl)silane (Sigma Aldrich) by placing a wafer in a desiccator with an open vial of trimethoxy(octyl)silane under low vacuum for three hours. The substrates are then sequentially rinsed with toluene, acetone, and isopropyl alcohol and dried with nitrogen.

3.2 EHD Flow Assisted Chemical Assembly of Nanoparticles onto Pillar Templates

Au nanoparticles with 40 nm diameter in colloid are synthesized using a seeded growth method[20] at a concentration of 0.2 mg/ml. Nanoparticles are functionalized with lipoic acid (Sigma Aldrich) by replacing the citrate solution with pH 11 water and adding 100 μM of lipoic acid in ethanol. After overnight treatment the nanoparticle solution is then washed with DI water and the concentration is maintained at 0.2 mg/mL. 3 mL of this solution is added to a clean 10 mL beaker and 60 μL of 20 mMol s-NHS (Sigma Aldrich) in DI water with 100 mMol MES buffer (Sigma Aldrich) is added to this solution and swirled. Subsequently 60 μL of 8 mMol EDC (Sigma Aldrich) in DI water with 100 mMol MES buffer is added and swirled.

The functionalized Au pillars on Si substrate, as the working electrode, is then placed in the nanoparticle solution 0.5 mm apart from a Pt mesh counterelectrode with 1.2 V bias across them for 1 hour at room temperature. The bias is then removed and the substrate is moved to the bottom of the beaker where subsequent dilutions of the nanoparticle solution are performed with 10 mMol NaCl solution until the solution is diluted 1000 fold. This is performed to minimize aggregation of nanoparticles on the surface due to drying effects. The substrate is then rinsed thoroughly with isopropyl alcohol as it is removed from solution and then quickly dried with nitrogen. Excess nanoparticles are then selectively removed by submerging the substrate in 5% methylamine solution and sonicated for 10 minutes.

3.2 Characterization

Scanning electron microscopy images are obtained with a Magellan (FEI) SEM. The optical responses of close-packed oligomers are understood with full wave electromagnetic simulations (CST).
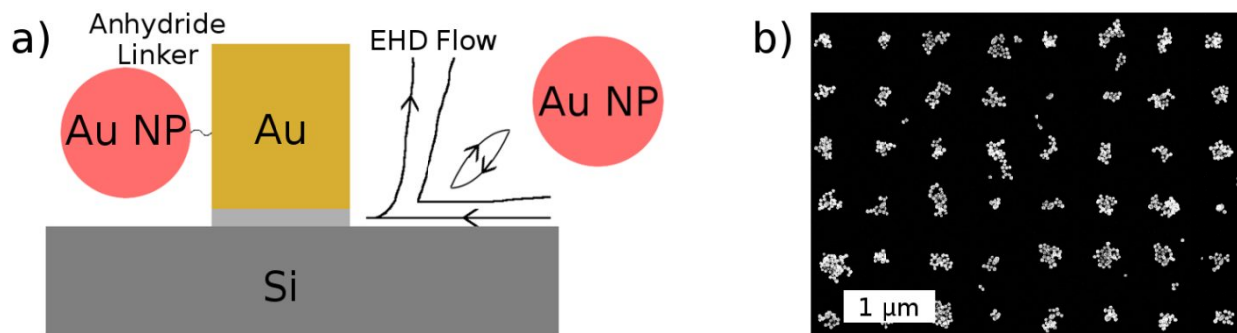
4. RESULTS AND DISCUSSION

Figure 2: a) Schematic of electrohydrodynamic nanoparticle assembly on block copolymer template. Inset depicts electrohydrodynamic flow fields generated by nanoparticles bound to the surface. b) Close-packed plasmonic metamolecule array fabricated via the method depicted in Figure 1 before chemical removal of excess nanoparticles.

Metamolecules composed of close-packed nanoparticles are assembled via a directed assembly approach. Electrohydrodynamic (EHD) flow enables carbodiimide crosslinking of nanoparticles to a template composed of Au nanopillar arrays. The EHD flow – crosslinking assembly system, depicted in figure 2 a, works as follows: a conductive substrate with Au nanopillars and counter electrode are placed in a carboxylic acid functionalized Au nanoparticle electrolytic colloid solution and a bias is applied across the electrodes. At the substrate surface, the ion double layer around a nanopillar is deformed by the applied bias resulting in an ionic concentration gradient. This concentration gradient results in lateral osmotic flows towards the nanostructure (equilibrium charge electroosmosis)

and the action of the double layer on the substrate's double layer also causes lateral osmotic flows towards the nanostructure (induced charge electroosmosis), the combined osmotic flows are called EHD flow. An additional induced charge electroosmotic flow is generated by the hydrophobic/hydrophillic interface between the amine terminated Au nanopillars and the alkane terminated Si surface. The Au nanoparticles are driven to the templated substrate due to electrophoretic sedimentation and are entrained by EHD flows generated by the nanopillars. This results in assembly around the pillar to form close-packed assemblies. When the field is removed, assemblies will rapidly dissolve into solution, so crosslinking is neccsary to "freeze-in" these assemblies for use in plasmonics.

In order to prevent the dissolution of the assembled metamolecules, chemical crosslinking is used to covalently bind the nanoparticles and nanopillars together. The carbodiimide activates the carboxylic acid moeities on the nanoparticles, forming O-acyliosureas that participate in crosslinking reactions. Two crosslinking pathways are possible: 1) the O-acylisourea attacks the amine groups on the nanopillars, linking the nanoparticles via an amide bond. 2) the O-acylisourea attacks the carboxylic acid group on the nanoparticles, linking together nearby nanoparticles via an anhydride bond. The latter process does not occur in solution due to the long timeframes necessary for reaction and is selectively enabled by the extention of the residence time of nanoparticles in assemblies generated by EHD flow. The result is permanent, anhydride linked, close-packed assemblies on a conductive substrate. The anhydride linker is a key advantage of this assembly system. Plasmonic systems with small gap spacings, or hotspots, are incredibly sensitive to variations of the gap spacings and lead to detuning of resonances that are a significant fraction of the resonance linewidth. Here, these gap spacings are controlled to the molecular level by chemical crosslinks.

Figure 2 b depicts close-packed metamolecules as assembled according to the methods section before methylamine treatment. The diameter of pillars ranges from 40-100 nm diameter with 50 nm height pillar arrays and 1 μm pitch. One may observe that the nanoparticle deposition is strongly effected by the EHD flow producing Au nanopillars. These assemblies are significantly larger than one ring around a pillar due to continued entrainment of nanoparticles into EHD flows and anhydride crosslinking of nanoparticles onto existing nanoparticles. The primarily two-dimensional character of these assemblies is due to the relative strength of the EHD flow fields which are lateral. Nanoparticles observed in the plane above the surface can be observed to be directly linked to pillars and are likely cuased by brownian motion or electrophoresis. Assemblies such as these contain magnetic resonances, but are clearly not uniform enough for plasmonic metasurface applications; further treatment of the substrate is necessary to achieve large area functional magnetic resonator surfaces.
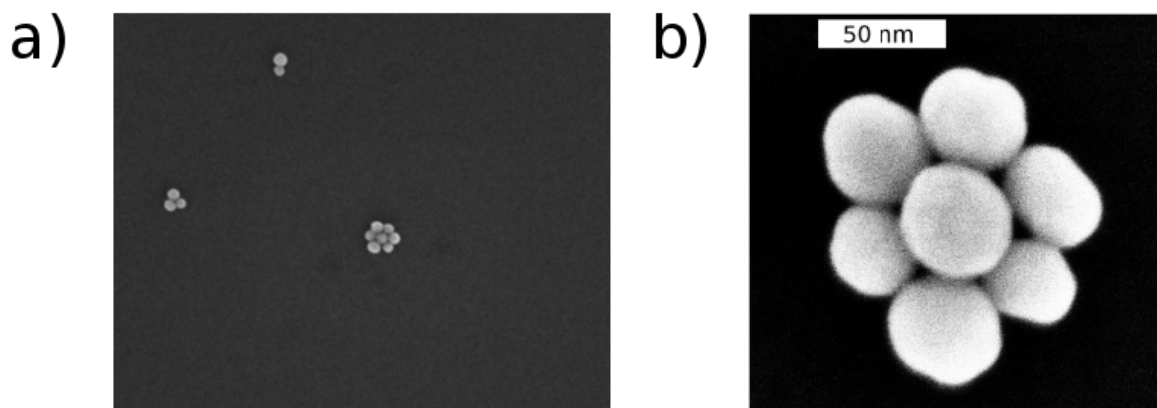

Figure 3: a) SEM micrograph of a close-packed metamolecule after methylamine treatment. b) Large magnification image of a close-packed metamolecule.

The dual pathway carbodiimide crosslinking enables the selective removal of nanoparticles that are not bound to pillars. Over-assembled metamolecules occur on the surface due to the continued entrainment of nanoparticles into EHD flow fields generated by the metamolecules and further anhydride crosslinking. Fortunately, the anhydride group linking nanoparticles may be attacked via nucleophilic substitution and cleaved, unlinking the nanoparticles, while the amide bond between particles and pillars is robust to nucleophiles. Figure 3 a depicts metamolecules after an assembled substrate is sonicated in 5% methylamine solution for 10 minutes. The process leaves pillar defined metamolecules significantly increasing the uniformity of the assemblies. Due to the close-packed assembly provided by EHD flow, proper design of the center pillar ensures uniform numbers of nanoparticles in a metamolecule, the gap spacing control – which may be observed in Figure 3 b – further ensures consistent spectral position of magnetic resonances exhibited by the metamolecules.
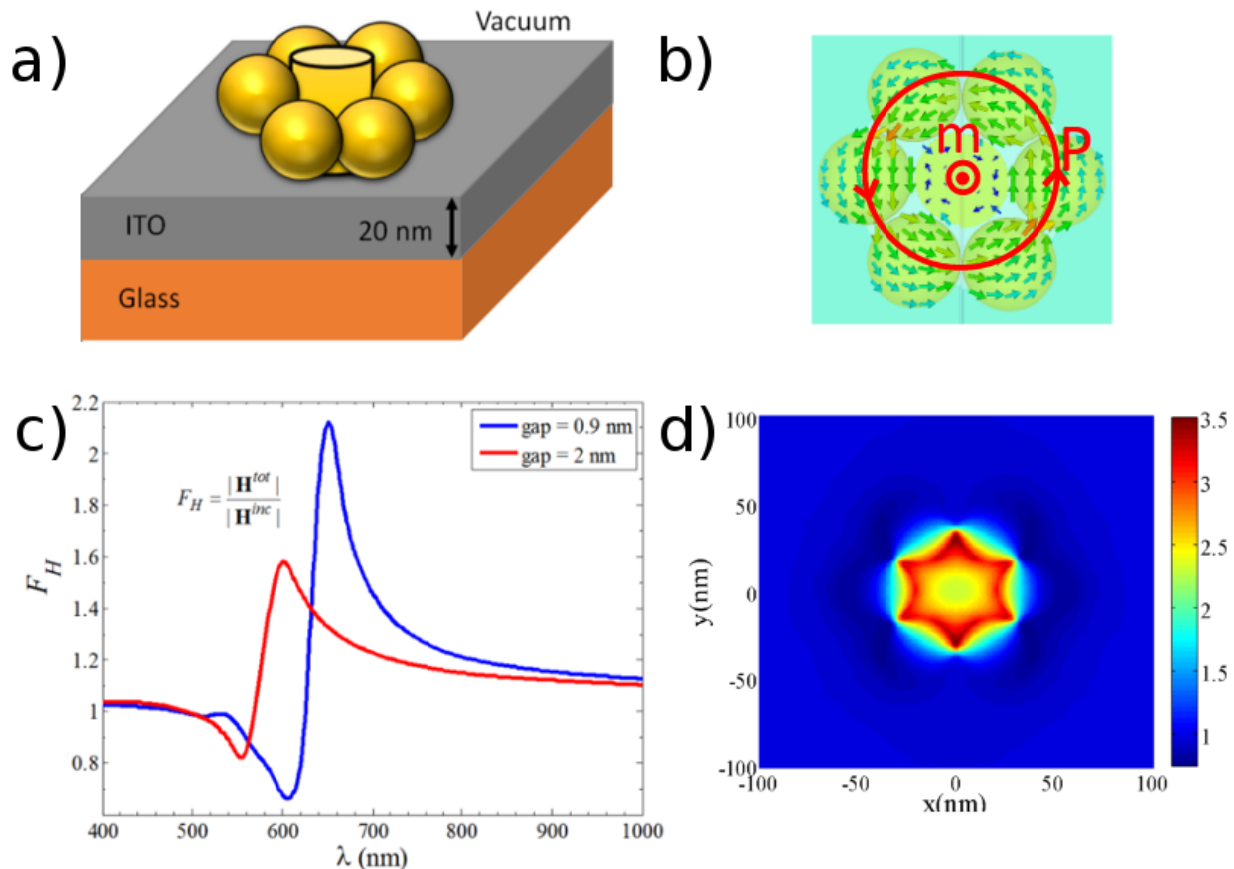

Figure 4: a) Schematic depicting nanoparticles assembled around a Au pillar defined with electron beam lithography on an ITO coated glass substrate. b) Full wave simulation plotting the current density distribution of the structure with a schematical representation of the polarization and magnetization produced by the close-packed metamolecule structure. c) Plot of the magnetic field enhancement F_H in the gap between two nanoparticles as a function of wavelength at two gap spacings. The small gap spacings that result from anhydride crosslinking are shown to significantly increase F_H. Both structures are shown to have magnetic resonances in the visible regime d) Full wave simulation depicting the magnetic field enhancement of the structure in Figure 2 c at a crossectional slice taken from the halfway point of the pillar height at the structure's resonance wavelength.

Having observed close-packed metamolecules, we turn now to consider their properties as magnetic resonators. Reflections from Si disrupt magnetic resonances so Figure 4 a shows six gold nanoparticles with diameter of 40 nm are placed around a pillar with diameter 40 nm and height of 50 nm on ITO coated glass, this

substrate is compatible with the assembly method outlined above. With excitation from two oblique plane waves at +/- 45^0 we observe, in Figure 4 b, circular currents that give rise to an orthogonal magnetism. This effect is a result of the six fold rotational symmetry where electric dipoles in individual Au nanoparticles hybridize with their neighbors to generate current distributions with the continuous symmetry of the metamolecule.

The magnetic field enhancement is defined as the ratio of the magnitude of the total magnetic field in presence of nanoparticles and pillar, to the magnitude of the incident magnetic field in their absences at the same location. Figure 4 c shows the magnetic field enhancement versus wavelength in visible and NIR region, for the structure shown in Figure 3b. Two gap spacings are analyzed to demonstrate the efficacy of using molecular linkers to build magnetic resonators. While artificial magnetism is an inductive effect and small gap spacings are typically used as capacitors in the context of metamolecules, we still observe a large increase from ~1.6 to ~2.1 of the magnetic field enhancement in the gaps between nanoparticles. This effect is due to the field confinement. Smaller gap spacings yield more strongly hybridized modes and thus lower energy, larger wavelength resonances. With the mode volume reduced somewhat with the smaller gap spacings and the wavelength made larger, the field confines more than compensates for the increased capacitance leading to larger magnetic field enhancements. In either case, one can observe a Fano lineshape of the response due to interference between the narrow magnetic resonance and the broad electric resonance. The narrow Fano-type magnetic resonance demonstrates the necessity of fine control over gap spacings between nanoparticles and the pillar, the small deviation from 0.9 nm to 2 nm leads to low overlap between the modes which would reduce device performance if the two metamolecules coexisted on the same surface.

Magnetic field enhancement profile, in the transverse cross section of the structure for 0.9 nm gap, has been shown in Figure 4 d. As it is clear from the figure, in the all gap spacings between nanoparticles and the pillar, magnetic field enhancement is strong. Unlike metamolecules for enhancing electric fields, we see that the magnetic field enhancement occurs over a large fraction of the metamolecule area. This enables sensors based on this technique to probe a significantly greater number of molecules than electric field enhancing resonators which may help compensate for the somewhat smaller field enhancements achieved by magnetic resonators.

5. CONCLUSION

In this work, we have demonstrated the importance of combining short range and long range driving forces in self-assembly of Au nanospheres from colloid. Nanoantenna surfaces composed of oligomers are formed using local chemical reactions and EHD flow that drives nanospheres together for the formation and retention of anhydride bridges. The anhydride linker is observed with surface enhanced Raman scattering spectroscopy and also shown to be cleavable via nucleophilic substitution. The process by which anhydride linkers are selectively promoted between particles on a substrate surface is elucidated via molecular dynamics simulations that demonstrate long residence times at small nanoparticle gap distances are necessary. The EHD flow – anhydride crosslinking directed assembly method is then used on Au nanopillar arrays to control the deposition of close-packed plasmonic metamolecules. The magnetic resonance of an individual metamolecule is investigated and shown via full wave electromagnetic simulations to enhance the local electric field by a factor of 3.5. These results represent a step towards sensing of molecules with optical magnetic moments over a large area.

6. ACKNOWLEDGEMENTS

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