SPECIAL SECTION: NANOMATERIALS

Giant single crystalline Au microplates

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Single crystalline Au(111) surface is the most sought after platform for studying molecular and other interesting phenomena. Here we report the synthesis of giant Au(111) single crystalline microplates along with their prototype applications. The single-crystal surfaces are atomically flat and possess areas extending over ~ 100,000 μm^2. The synthesis method is simple involving a one-step thermolysis process, i.e. heating on a hot plate, of a alkylammonium salt, making the process flow easy and scalable for mass production. Other interesting anisotropic structures such as nanorods and microstars are also obtained by slightly varying the synthetic conditions.

Keywords: Gold, microplates, single crystals, synthesis.

WELL-DEFINED metal surfaces are important in studying any surface phenomenon such as surface reactions[1], reaction kinetics[2] and catalysis[3], molecular self-assembly[4], etc. Such surfaces are usually obtained by cutting and polishing metal single crystals[5] to specific crystallographic orientations or by growing oriented thin films[6] either chemically or by physical deposition methods. While surfaces of transition metals have been extensively employed for surface reaction studies, the Au(111) surface has attracted unprecedented attention because of its use in molecular self-assembly[7]. But Au single crystals are not easily affordable, due to which usually thin, oriented Au(111) films are always preferred for routine use. Conventionally used Au(111) substrates are derived from bead crystals produced by resistive heating[8] or by flame annealing of the thin films of polycrystalline Au[9]. But both require high-temperature processing and in addition require large amounts of the raw metal. Other methods for Au(111) include templated stripping of flame-annealed Au[10] and acid treatment of Au surface[11]. However, it is not trivial to produce flat, clean, atomically smooth Au(111) surfaces as substrates for instance, for use in scanning tunnelling microscopy (STM) imaging, by any of these methods. STM studies therefore rely on other substrates such as highly oriented pyrolitic graphite (HOPG), which provides atomically smooth and clean surface just by peeling. HOPG being chemically inert, surface functionalization is rather difficult. Thus it is of paramount importance to develop methods to produce

large, flat smooth Au(111) surfaces on a routine basis. We have come up with a process which makes use of simple, chemical Au organic precursors, involving alkylammonium phase-transfer agents.

Albeit the known use of quaternary ammonium salts with metal anions in the extraction of metals from aqueous solutions[12,13], it is far less explored in materials research. One noteworthy example from the literature has been the Brust method[14], where $(AuCl_4)^-$ ions extracted using tetraoctylammonium bromide (ToABr) in toluene were employed for controlled synthesis of alkanethiol-capped Au nanoparticles. Recently, we have reported[15] that the Au–ToABr precursor (i.e. $(AuCl_4)^-$ ions stabilized by ToABr in toluene) upon thermolysis gave rise to Au microplates having edge lengths of 100 μm with areas up to 12,000 μm^2. Subsequently, we studied the growth mechanism of these microplates using detailed *in situ* microscopy[16]. With the quest for obtaining giant Au microplates, we have recently optimized the recipe. In this article, we report the formation of very large Au microplates extending up to sub-millimetre sizes and possessing areas of ~ 100,000 μm^2, and study the utility of the giant microplates in various applications.

The synthesis consists of a simple single-step thermolysis of phase-transferred Au–ToABr precursor. Freshly prepared Au–ToABr precursor solution (100 μl, 200 mM) was drop-coated onto a well-cleaned, thin glass slide and heated at 130°C in air on a hot plate for 55 h (Figure 1 *a*) to produce large Au single crystals.

After thermolysis, the unreacted Au–ToABr was washed-off in toluene. Figure 1 *b* shows several microplates covering the substrate, with the magnified images of single Au microplates shown in Figure 1 *c* and *d*. The Au microplates thus formed are visible even to the unaided eye. The plates exhibit polygonal morphology; many appear as hexagons and truncated triangles. These microplates possess areas ~ 80,000 to 100,000 μm^2, i.e. ~ 0.1 sq. mm, significantly larger than the ones previously reported by us[15] with areas below 12,000 μm^2. In terms of synthesis, the present method differs in certain parameters from the one reported earlier[15], in that, keeping the thermolysis temperature as low as possible, i.e. at 130°C, the annealing time was increased from a few hours to a few days. The slower kinetics seems to play an important role in yielding larger microplates. Also, the concentration of the precursor does not proportionately increase the size of the microplates; instead there was an optimum concentration,

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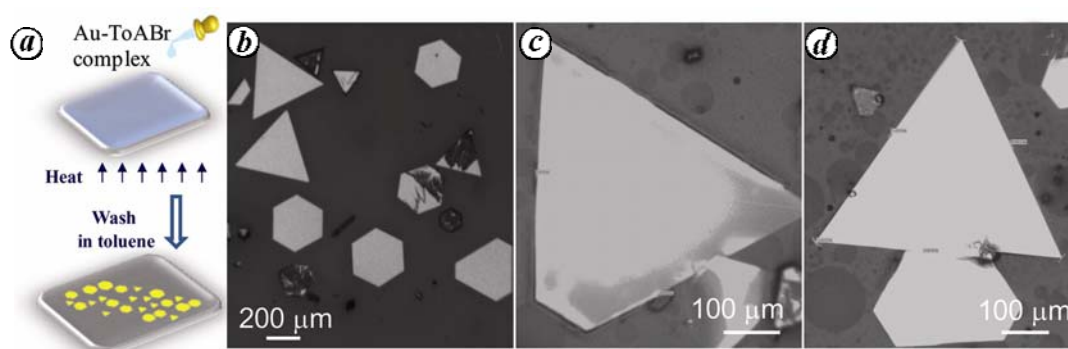
Figure 1. Giant Au microplates. *a*, Schematic of the synthesis of Au microplates. *b*, Optical images of the as-synthesized microplates. Dark traces on some of the microplates are due to the unreacted precursor. *c* and *d*, Magnified images of the giant Au microplates. Thermolysis was done at 130°C for 55 h.
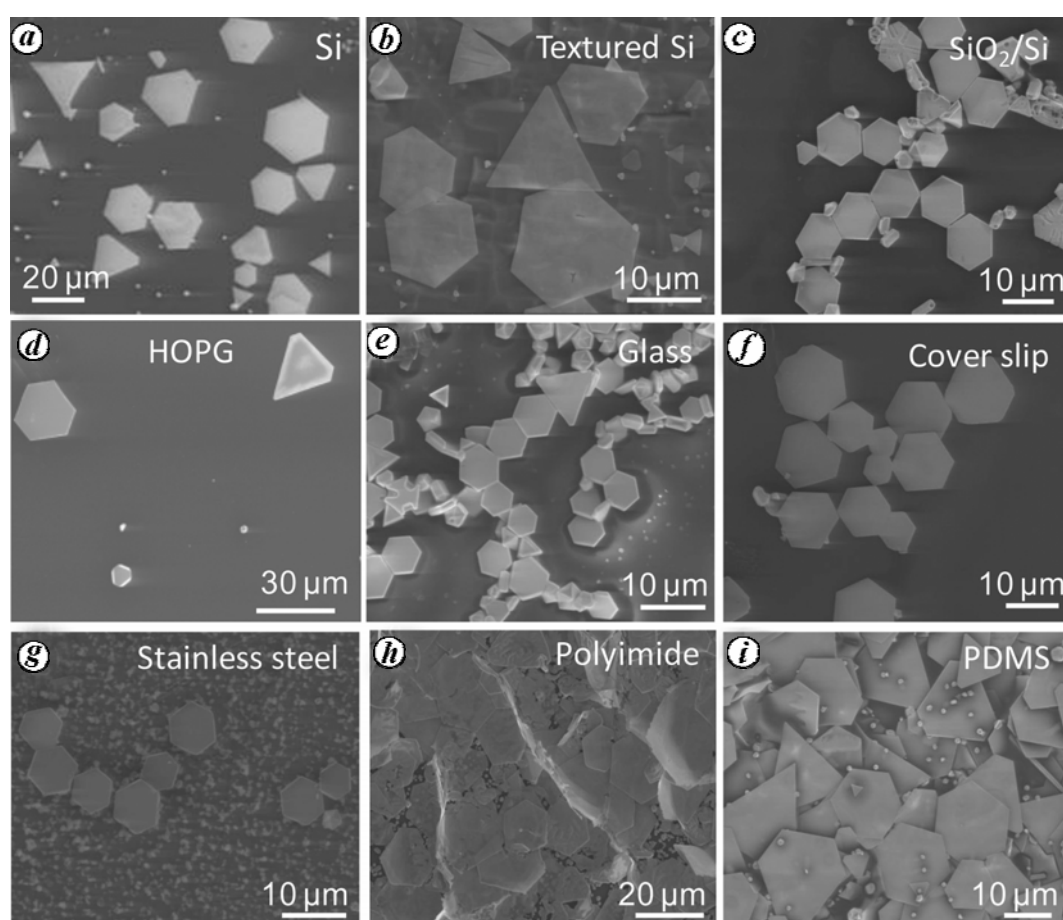
Figure 2. SEM images of the Au microplates synthesized on various substrates, indicated over the image. Thermolysis was done at 250°C for 3 h.
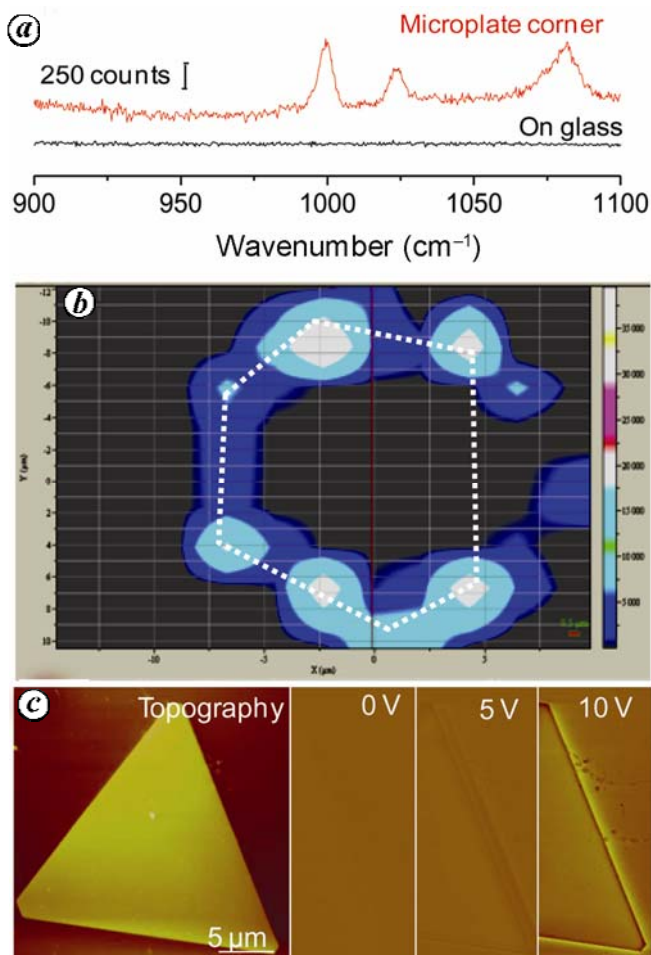
i.e. 200 mM above or below which smaller microplates were obtained. Importantly, we have found that a freshly prepared Au–ToABr solution unexposed to ambient light is much more effective than an aged solution left in the ambient. As is well known[17], aged $(AuCl_4)^-$ solutions contain some reduced Au species which may follow a different trend of growth than those from the molten precur-

sor and in effect, hinder the latter growing into large-sized single crystals.

The synthesis of the Au microplates can be carried out on various substrates, such as Si, glass, stainless steel, polyimide, polydimethylsiloxane (PDMS), mica, HOPG, etc. In fact, almost any substrate that can stand the thermolysis temperature and remain insoluble in the solvent

(i.e. toluene) can be used. Figure 2 shows the scanning electron microscopic (SEM) images of the Au microplates synthesized on various substrates, at a thermolysis temperature of 250°C for 3 h. Notably, even on a rough surface such as textured Si, Au microplates could grow but with small cracks on the surface. Among others, Si and coverslip substrates prove to be the best for growing giant, unbroken Au microplates with good yield (Figure 2).
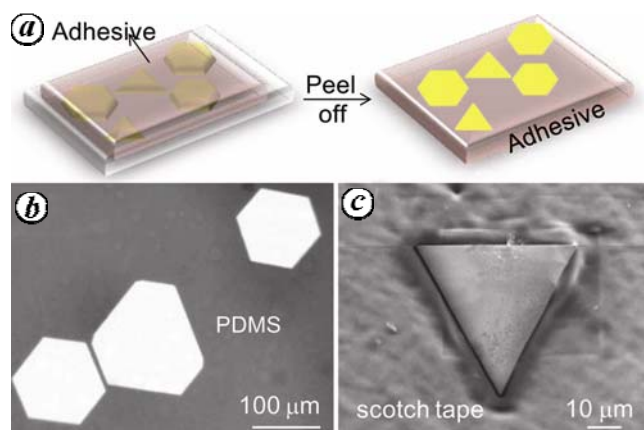
Au being a plasmonic metal, we considered it interesting to study the prospects of using the surface of the microplates for surface-enhanced Raman spectroscopy. For this purpose, a 1 mM solution of a Raman marker (thiophenol) was chemisorbed onto the surface of a hexagonal microplate by self-assembly. Raman spectrum recorded on the corners of the microplate is shown in Figure 3 a, along with that recorded on the glass slide coated with 1 mM thiophenol solution. Figure 3 b shows

the Raman mapping of the 1000 cm^{-1} peak across the entire Au microplate surface. Owing to the smoothness of the Au microplate, there was no enhancement at the centre of the microplate, and the enhancement in the Raman signal was clearly evident only at the corners. In order to understand this phenomenon, electrostatic force microscopy (EFM) was performed on the Au microplates (Figure 3 c). EFM measures local electrical properties by measuring the electrostatic force between a biased AFM tip and the sample surface[18]. Figure 3 c shows the topography image of a Au microplate. While applying different bias values, EFM images were recorded at a lift height of ~ 150 nm, as shown in Figure 3 c. With increased tip bias, i.e. at 10 V, we see the edges and corners of the microplate appear brighter (with either positive or negative bias), indicating a higher electric field in those regions. This observation agrees well with the literature reports[19] that along the sharp edges and corners of metal nanostructures, there will be an enhanced electric field and hence enhanced Raman signal.

As-synthesized Au microplates are transferrable to other substrates, which is important in properties such as site-selective wettablity, cytophilicity, etc. Here we show how Au microplates could be embedded in a polymer matrix. The process of doing so is explained in Figure 4 a. The polymer chosen here was PDMS, which is extensively used as a biomaterial in ear and nose implants, pacemaker insulation, catheters, drainage tubing, for membrane oxygenators, etc.[20]. In the recent past, use of PDMS for replicating nanostructures with high fidelity is well acknowledged and it forms the heart of a branch of lithography named soft lithography[21]. PDMS elastomer mixed with curing agent was poured over the microplates on a given substrate and the entire set-up was kept in an oven at 50°C overnight for curing the PDMS. After

Figure 3. *a*, Raman spectrum of thiophenol chemisorbed on a Au microplate, recorded on a corner. *b*, Raman mapping of 1000 cm^{-1} peak recorded on the hexagonal microplate (shown as dotted line). Corners show enhanced Raman signal. *c*, EFM data. AFM topography image of the Au microplate and the corresponding EFM images at 0, 5 and 10 V respectively. For EFM, a biased conducting tip coated with a 20 nm layer of Pt/Ir evaporated on top of a thin 3 nm Cr adhesion layer was used. The lift height was 150 nm.


Figure 4. Transferability of Au microplates to other substrates. *a*, Schematic illustration of the process; The adhesive, i.e. either a scotch tape or a polymer such as PDMS which can be cured, is brought over the microplates on a substrate and peeled off. *b*, Optical image (in reflection mode) of the cured PDMS peeled-off from the substrate. *c*, SEM image showing the faithful transfer of Au microplates to the scotch tape.
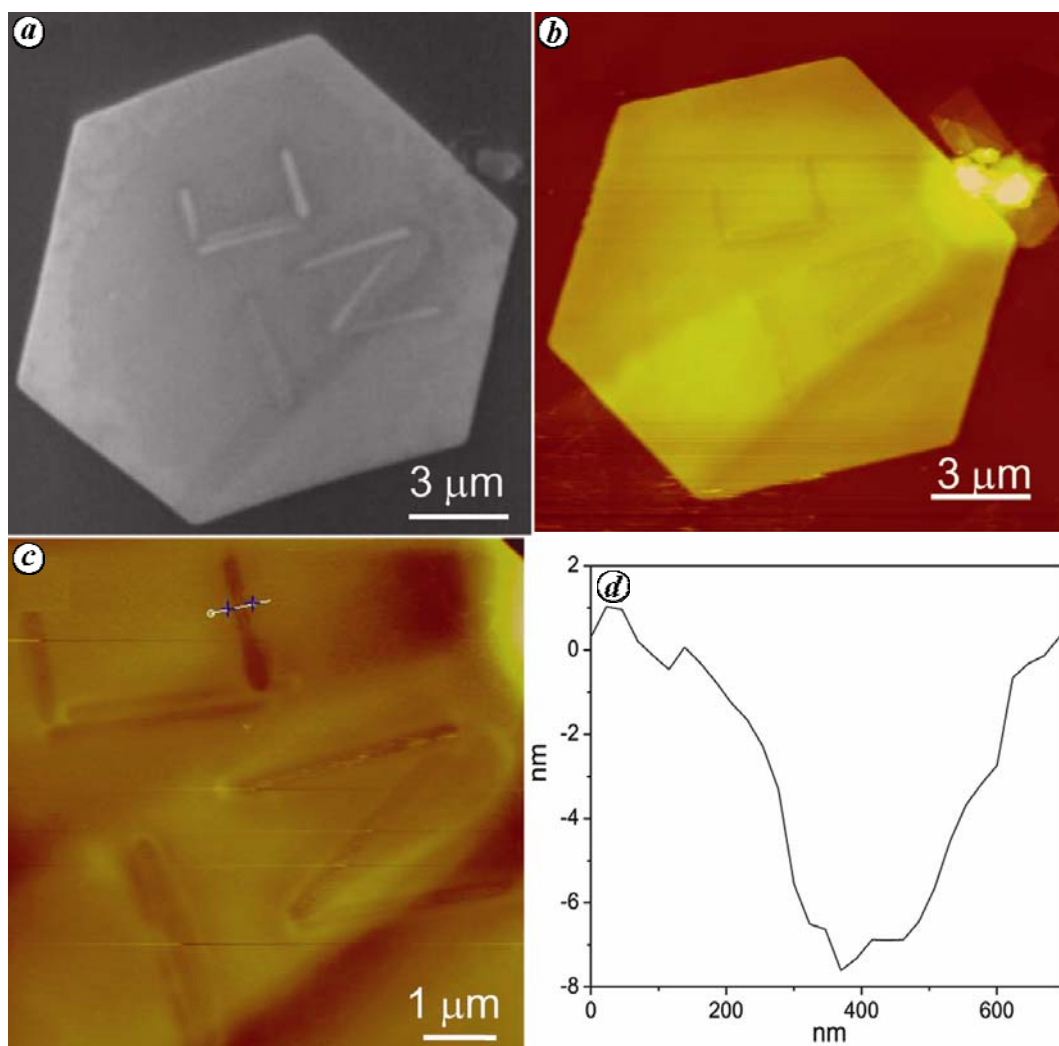
Figure 5. SEM (*a*) and AFM (*b*) images showing the nanotrenches in the form of alphabets made by EBL (10 kV, 0.6 mC/cm) on Au microplate surface. (*c*) Magnified AFM image and (*d*) the corresponding *z*-profile.

cooling to room temperature, cured PDMS was peeled-off from the substrate, leading to Au microplate-embedded PDMS (Figure 4 *b*). PDMS hosting Au microplates presents a unique platform for hosting live cells, as the cells can be selectively adsorbed only onto the microplates as the microplate surface is cytophilic[15] while the PDMS surface, as known[22], should inhibit cell adhesion. Additionally, the microplates carrying cells can enhance fluorescence signal used as label. Instead of PDMS, the Au microplates can also be transferred to a scotch tape by simply peeling them off from a glass or Si substrate (Figure 4 *c*).

There are other possibilities relevant to technological applications. We have attempted nanopatterning on the surface of the microplates. Ion beam milling of metal surfaces to create nanoelectronic circuits is well-documented[23]. Au nanoplates have also been milled through ion beam to produce nanocomponents such as nanowheels[24] and nanoresonators[25]. Recently, plasmonic nanocircuits

such as nanoantennas have been realized on single-crystal Au microplates by focused ion milling[26]. Here, we propose that our giant Au microplates could also be used efficiently for producing high-quality single crystalline components. In Figure 5, we show that, even a low-energy electron beam (5 kV) is able to create trenches on a Au microplate surface. The trenches created were about ~ 7 nm deep.

Since the Au microplates can enhance fluorescence of dyes, we extended the utility now to enhancing the fluorescence of molecular crystals. In general, organic fluorophores display very low quantum yield in the solid state. Strong fluorescence in solid state is important if one wants to use such molecules in device applications. A concept experiment of fluorescence enhancement for molecular crystals is demonstrated using 1,4-bis(phenylethynyl)-2,5-bis(*n*-propoxy)benzene as a model system. Crystals of this molecule are known to exhibit fluorescence around 515 nm in the solid state, with a high
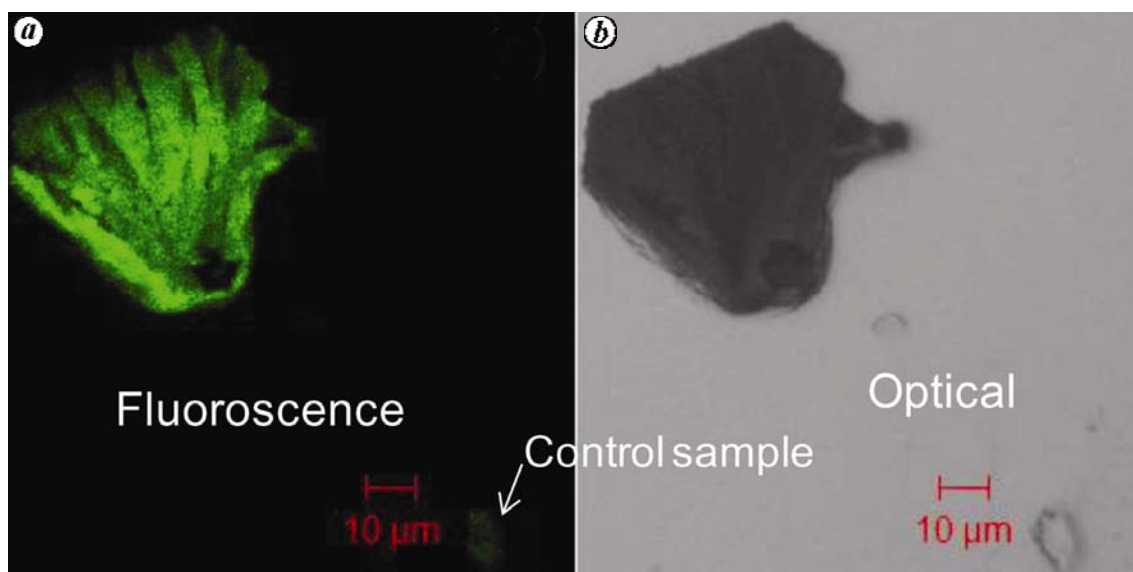
Figure 6. Metal-enhanced fluoroscence: Dark field confocal (*a*) and optical images (*b*) of an organic fluoroscent crystal (oligo(phenyleneethynylene)) on a Au microplate.
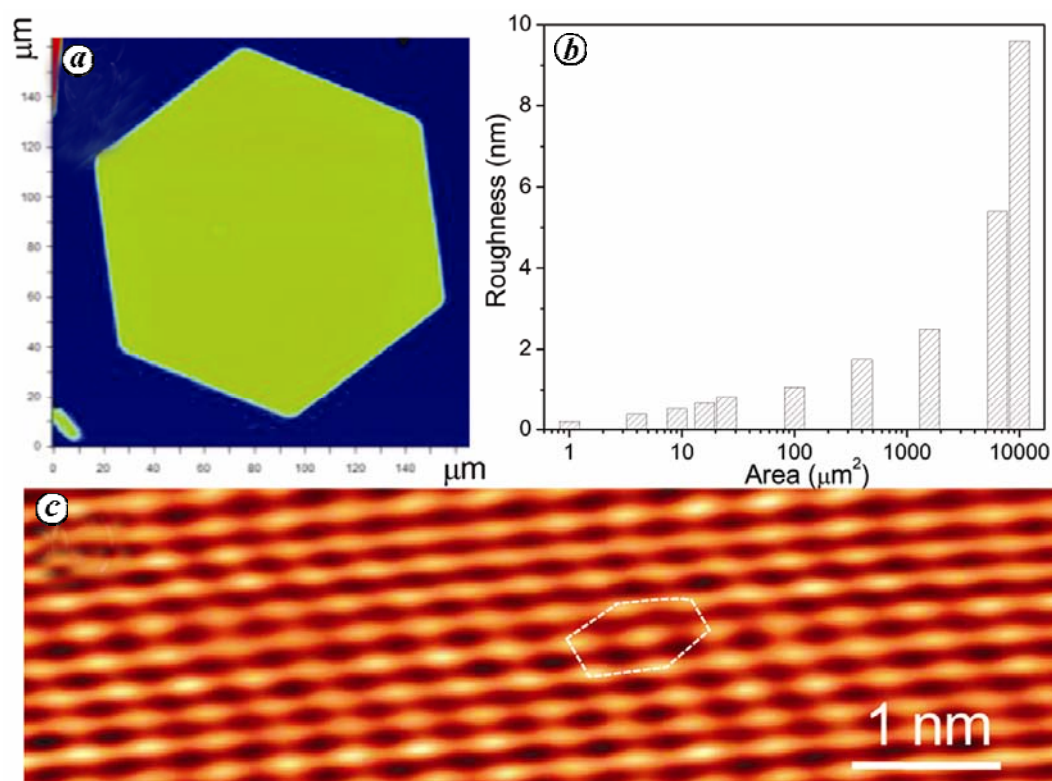
Figure 7. Ideal scanning probe microscopy substrates: *a*, Optical profilometric image of Au microplates. *b*, Average roughness versus area from which roughness was calculated. *c*, STM image of a Au microplate, showing typical (111) orientation (see dotted line). The image was recorded using a Bruker diInnova Scanning Probe Microscope with Nanodrive controller. Pt–Ir precision-cut wire (model no. CLST-PTBO) of 0.5 mm diameter and 20 mm length was used as a tip. The noise and drift in the image are due to the instrument instability.

quantum yield of 0.53 (ref. 27). A crystal was grown on Au microplates by drop-casting a toluene solution of the molecule onto Au microplates. Slow evaporation of the solvent at room temperature led to crystal growth on the microplate surface (Figure 6). Confocal imaging of the crystals on Au microplates showed enhanced fluorescence compared to the ones grown on glass slide as control. Although the distance between the molecular crystal
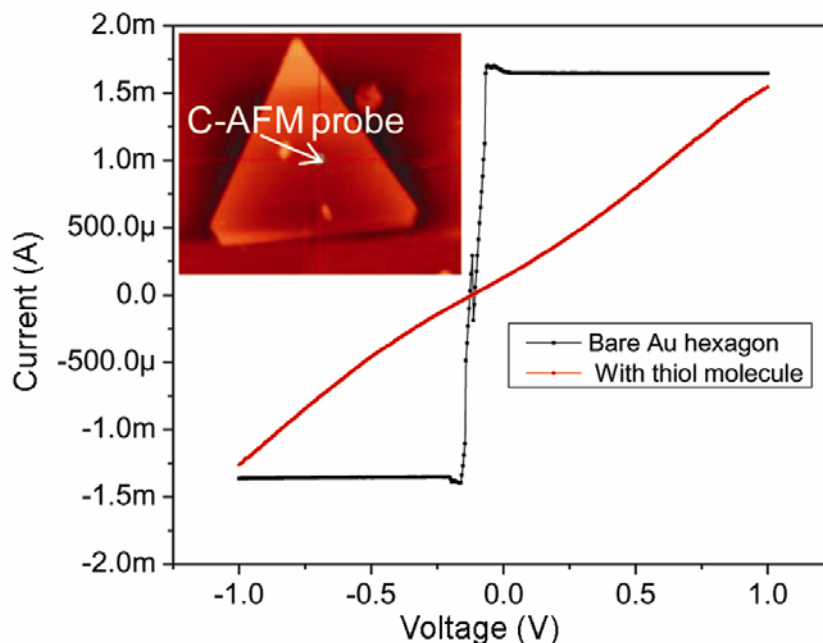
Figure 8. Current–voltage characteristics recorded by C-AFM of Au microplate placed on a HOPG substrate: *I–V* data recorded on a microplate chemisorbed with dodecanethiol molecules (red) and those on the microplate without any molecules (black). (Inset) image of the microplate and position of the C-AFM probe.

and Au microplate is small enough to cause quenching of luminescence due to charge-transfer interactions, we still observe enhancement in fluorescence. In general, metal-enhanced fluorescence is observed only when there is a spacer between a dye film and the metal. Here, it might be explained that the crystal has thickness more than a few micrometres. So, even if the surface of the fluorescent crystal is in contact with the Au microplate, maximum portion of the crystal is at a distance, which could lead to enhancement. Thus, we can envisage that the solid-state quantum yield of industrially important organic molecules can be increased using Au microplates as platforms.

The microplates synthesized by the current technique have some unique properties – large, flat, clean and self-supporting and movable – thus presenting them as ideal scanning probe microscopy substrates. First, as mentioned earlier, Au microplates are atomically smooth (surface roughness < 1 nm over tens of micrometres; see Figure 7 *a* and *b*). They are easily identifiable on a given substrate owing to their large size. The microplates being made up of Au, can be easily functionalized. Further, the microplates are amenable for manipulation. The STM image from Au microplate surface obtained in a preliminary study is shown Figure 7 *c*. Another potential application of these microplates is to serve as molecular electrodes (Figure 8). Here we have shown large-area molecular electrodes using conducting-AFM (C-AFM) as probe. A microplate attached with dodecanethiol molecules in the form of a self-assembled monolayer (SAM) was placed on a HOPG substrate. The *I–V* data (Figure 8)

are nonlinear, typical of alkanethiol molecules. Knowing the area of the microplate ($52.9\ \mu m^2$) and the density of the SAM[28] ($4.67 \times 10^{18}\ mol/m^2$), the resistance per molecule was calculated based on the resistance near zero-bias ($892.8\ \Omega$). The resistance per molecule works out to be $220\ G\Omega$, close to literature values[29]. When the tip was placed on another microplate, which was not covered with the SAM, the *I–V* data showed a linear behaviour as expected.

Au–ToABr precursor can also be used for obtaining other interesting anisotropic structures. When the thermolysis of the precursor was carried out on a substrate in a heat-confined environment (i.e. by placing a cured PDMS flat piece on top of the precursor film on a substrate), microstars were obtained instead of microplates (see Figure 9 *a* and *b*). In another instance, the synthesis of Au–ToABr precursor itself was modified. Instead of using $HAuCl_4$, the aqueous $(AuCl_4)^-$ solution was obtained starting with an Au foil and dissolving it in aqua regia, and water was added to make up to the required concentration. This was phase-transferred to toluene using ToABr, as usual. A 25 mM solution of the phase-transferred Au–ToABr was drop-coated on a substrate and thermolysed at 130°C for 55 h. In this case, the synthesis ended up with Au nanorods instead of microplates. The nanorods were ~70 nm in diameter and ~100 μm long (see Figure 9 *c* and *d*).

The scope of the microplates bearing such unique properties as shown above, is exciting. Thus, for instance, the process flow of making the STM substrate is to simply drop-cast the Au microplates dispersed in toluene
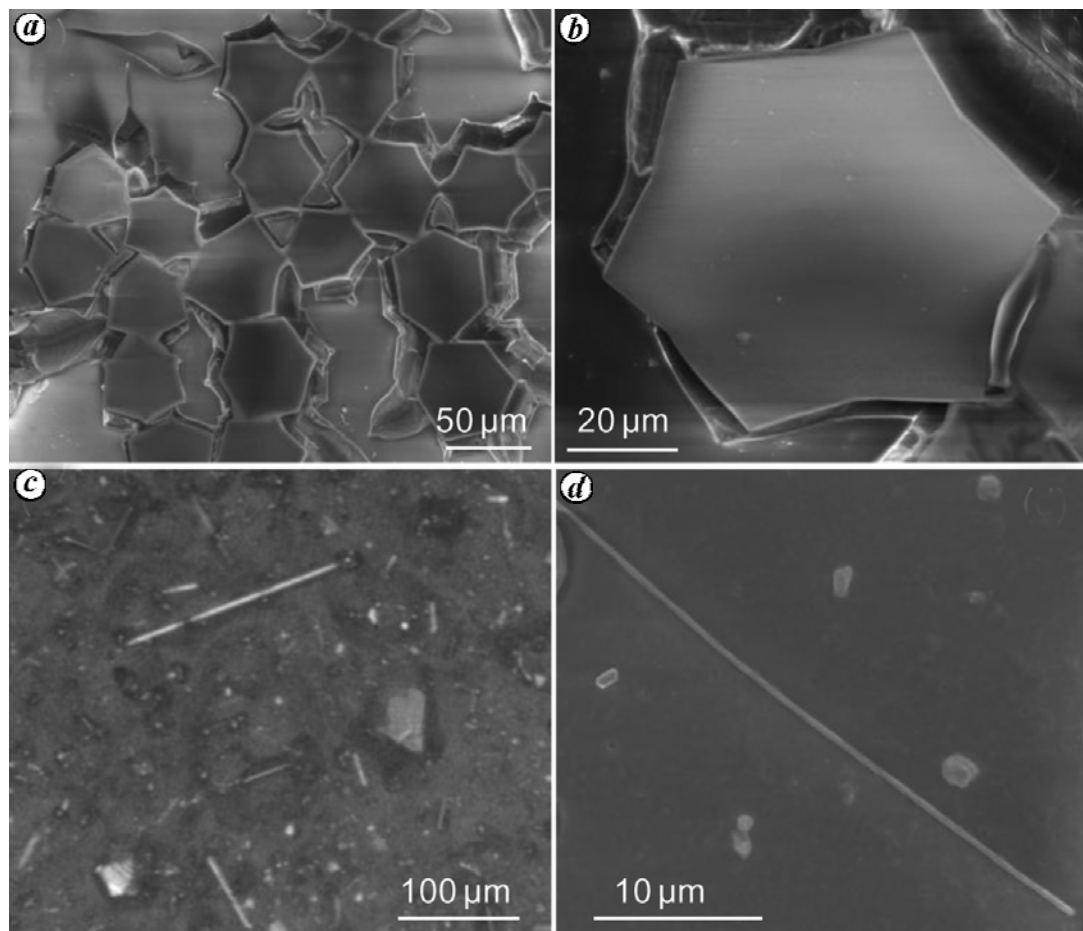
Figure 9. Other interesting anisotropic structures: *a*, SEM image of the Au microstars synthesized by confined heat treatment of Au–ToABr, *b*, magnified image of a single microstar. *c*, Au nanorods obtained from modified Au–ToABr precursor and; *d*, magnified image of a single nanowire.

onto any conducting base substrate such as a thin film of metal, indium-coated tin oxide, HOPG, stainless steel, etc. The plates of desired size can be obtained by arresting the growth at any instant, by simply turning-off the hot plate and cooling to room temperature. Further, a halted process can be regained for further growth, if required, provided the substrate containing unreacted precursor is left undisturbed.

Using these microplates as STM substrates, one can envisage studying even complex molecular transformations and reactions between individual molecules. For instance, Au microplates can be individually functionalized with different probe molecules, A and B. As the plates are movable, the microplates can be brought together using a simple manipulator. If there is any interaction between the probe molecules A and B, the edges of the microplates would be the first place for the initiation of the reaction, which can be dynamically captured by STM imaging or by SERS. Importantly, the choice of the base conducting substrate is not limited and it need not be atomically smooth as the roughness of the substrate is, in general, not reflected on the Au microplates. The applications are abound and exotic, such as making a sandwich device with two Au microplates with molecules captured in-between, microplates as electrodes for micro-capacitor, etc.

In conclusion, we have reported a simple, single-step synthesis of giant Au microplates. These single crystalline microplates can serve as STM substrates and save the tedious process of processing atomically smooth substrates. The process of electromagnetically enhanced SERS along the edges and corners of the microplate was clearly evident, which was supported further by EFM measurements.

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