Direct Micromolding of Bimetals and Transparent Conducting Oxide Using Metal–TOABr Complexes as Single-Source Precursors

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ABSTRACT: Patterning of metals, alloys, and conducting oxides is vitally important for many industrial applications pertaining to many technological devices. In this report, we have used the metal anion alkyl ammonium complex (M−TOABr) as a single-source precursor to obtain thin films as well as micro (μ)-patterns of bimetals (Au−Pd, Au−Pt, Au−Cu, and Pt−Pd) and conducting oxides (ITO). This complex can be easily filled inside the soft mold and converted to the desired material in a single step known as direct patterning. The as-obtained μ-pattern comprises a well-connected network of nanocrystals giving rise to metallic conductivity. These periodically aligned bimetals and transparent conducting oxide (TCO) microwires could effectively serve as electrodes as well as an electrocatalyst with the prudence of providing passage for light transmission for many functional photoelectrochemical devices. In addition, the electrochemical stability of the bimetallic film was examined by fabricating a supercapacitor device and by studying its performance.

INTRODUCTION

Alloys and bimetals of noble metals are immensely useful for various applications such as catalysis, optics, and magnetism over monometallic counterparts, owing to their improved performance and stability. Especially, nanoparticles of bimetals and alloys, which possess high surface area, have been the most sought after because of the synergy between the metals. For instance, alloy Au−Cu nanoparticles have been preferred over Cu nanoparticles because of their enhanced oxidation stability. In catalysis, the immobilization of catalysts on the solid support attracts huge attention, as it is highly desirable for one-pot cascade reactions. Conventional drop casting or spin coating of premade catalyst nanoparticles leads to the aggregation and reduction of the available active surface area. Also, the capping agents required for stabilizing the nanoparticles in solution are hard to get rid of after deposition onto the solid supports. It would be ideal to grow the nanoparticles on the support substrate to fix them firmly without capping agent contaminants and the particle aggregation. This, in general, is a tedious process requiring molecular inks or metal−organic precursors with optimum decomposition temperature, as it yields catalytic particles free of capping agent directly on the desired solid surface. Metal−oleate and metal−thiolate complexes are few examples of such molecular inks used for the direct synthesis of nanocrystals of copper, nickel, bismuth, and palladium through simple thermolysis. Although single-source precursors of few metals are known in the literature, such methods are relatively less explored for bimetals, alloys, and conducting oxides. The double complex salts [M(NH3)4][Co(C2O4)2] have been used as a single-source precursor for the synthesis of Co−Pd and Co−Pt nanoalloys, but the obtained products were in the form of powder. On the other hand, while using the heterometallic complexes, carbon-supported bimetallic Pd−Bi and Pt−Ni nanoparticles were obtained.

Visibly transparent substrates coated with transparent conducting oxides are a vital component for various optoelectronic devices such as LEDs, liquid crystal displays, photovoltaic devices, and touch sensors as it combines optical transparency with controllable electrical conductivity. Tin-doped indium oxide (ITO) is a well-known optically transparent and electrically conducting oxide, which is widely used in many optoelectronic applications. The ITO thin films were usually fabricated using techniques such as magnetron sputtering, pulsed laser deposition, thermal deposition, and chemical vapor deposition. Although these processes yield large area electrodes with good optoelectronic properties, the process cost remains high as it involves high vacuum deposition conditions and importantly because of the wastage of about >50% precursors while deposition. To keep the process cost low, various attempts have been made to realize ITO thin films through solution processes namely sol−gel, spray pyrolysis, and so forth. However, preparing ITO thin films and its grating structures using single-source precursors are still obscure.

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Achieving the patterns of the active material into size and shape-controlled structures is important because properties mainly depend on the size and shape of nanomaterials.\textsuperscript{23–26} There are efforts in the literature to create the patterns of Pd and Pt using metal–organic precursors such as Pd thiolate,\textsuperscript{11} Pt carboxyl cluster,\textsuperscript{27} and so forth. Ideally, the versatility of patterning depends on the availability of appropriate ‘ink’ to yield the desired features. In recent times, many lithographic techniques have emerged to create patterns of materials.\textsuperscript{28–33} Among them, soft lithography is a simple method to produce patterns over a large area with a minimal number of steps. Furthermore, the process is quite economical, as it involves only the simple patterned elastomeric material namely PDMS (polydimethylsiloxane).

Here, we report the direct micromolding of bimetals such as Au–Pd, Au–Pt, Au–Cu, and Pt–Pd and transparent conducting electrodes by using the metal anion alkyl ammonium complex precursor as a direct-write precursor, which can be easily converted to the desired material in a single step known as direct patterning. Even though the complexation of metal anions with quaternary ammonium salts is well-known in the literature for extracting metals from aqueous solution,\textsuperscript{34,35} these precursors have not been explored as lithography precursors for transparent metal oxides such as ITO and bimetals. We have obtained bimetallic nanoparticles of gold (Au) in conjunction with metals such as palladium (Pd), platinum (Pt), and copper (Cu) directly on the glass or silicon substrates (although the method is not restricted to only these substrates). These bimetal combinations are prone to have interesting electrical, optical, and chemical properties than their monometallic counterparts. The chemical stability of the formed bimetal film was illustrated through the performance of a supercapacitor device fabricated using Au–Pd electrodes. Besides producing patterns of bimetals, efforts have been made to create μ-gratings of the transparent conducting oxide (ITO).

## RESULTS AND DISCUSSION

The methodology followed here begins with the phase transferring of metal anions (e.g., AuCl\textsubscript{4}–) to the toluene medium from the aqueous layer using TOABr, which acts as the phase transfer reagent (see Figure 1). The complex is quite stable in air and can be stored in an airtight dark container. To fabricate thin films of bimetal or transparent oxide, the phase-transferred organic layer was drop cast on the substrate, followed by thermolysis at the recommended temperature and atmosphere (see Table 1). As the interaction between the metal anion and TOABr is completely electrostatic, it is rather easy to separate metal from TOABr through thermolysis.

Among the bimetallic nanoparticles, Au–Pd is one of the interesting systems mainly because of its catalytic application in various organic reactions. The current synthesis approach begins with the simultaneous phase transfer of Au and Pd metal ions to the toluene medium followed by the thermolysis of metal–organic precursor on the glass substrate. Figure 2a–d shows the X-ray diffraction (XRD) patterns of the as-obtained products of Au, Pd, and its combinations annealed at 250 and 500 °C, respectively. The XRD patterns of the Au and Pd (Figure 2a,d) matches well with the corresponding standard patterns. The bimetallic film annealed at 250 °C (Au–Pd–1) clearly shows the XRD peaks corresponding to both Au and Pd (Figure 2b), whereas the film annealed at 500 °C (Au–Pd–2) (Figure 2c) matches with the intermetallic compound. Figure 2e,f shows the scanning electron microscopy (SEM) images of the Au–Pd film thermalized at 250 °C. The film is composed of highly interconnected hexagonal and a random-shaped particle network of Au–Pd embedded in the carbon matrix of a decomposed organic precursor (see the marked regions in Figure 2f). It is quite different in the case of the 500 °C annealed film. While annealing at the high temperature, leftover carbon vanishes leaving behind pores in the film (Figure 2g,h). It is well-known that properties of bimetallic nanoparticles not only depend on shape and size but also the distribution of metals at the surface. Thus, to confirm whether Au and Pd components are closely mixed or left segregated, we performed EDS mapping of Au–Pd thin films.

Similarly, different bimetal components such as Au–Pt, Au–Cu, and Pt–Pd have been prepared by mixing two metal anionic precursors while phase-transferring followed by annealing under the prescribed conditions in Table 1. The obtained thin films were analyzed using XRD, SEM, transmission electron microscopy (TEM), and EDS to confirm their crystal structure and component distribution (see Figures S1–S4 in the Supporting Information). The resistivity of the various bimetal thin films was measured and shown in Figure S5 in the Supporting Information.

To demonstrate the capability of the formed Au–Pd–2 film toward energy storage, a simple supercapacitor device was fabricated and its stability was tested. Upon thermolysis of Au–Pd TOABr at 500 °C for 30 min, it leads to the formation of Au–Pd nanoparticles embedded in functionalized amorphous carbonaceous species. The EDS spectrum confirmed the presence of carbon in the range of 35–40 at. %. It is known in the literature that this functionalized carbon plays a significant role in enhancing the performance of the supercapacitor.\textsuperscript{10} A symmetrical supercapacitor was formed by sandwiching two similar Au–Pd–2 electrodes with a filter paper as a spacer in between (Figure 3a inset). The electrochemical performance was characterized using a cyclic voltammogram and charge–discharge (CD) measurements. The CV of the device was performed at various scan rates ranging from 20 to 100 mV s\textsuperscript{–1}. The curves obtained are nearly rectangular, depicting the capacitive nature of the electrodes (Figure 3a). Figure 3b

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**Figure 1.** (a) Schematic illustration of the phase transferring of metal ions to an organic medium from the aqueous medium using TOABr (phase transfer agent). (b) Schematic showing the process of thin-film formation of bimetals and transparent conducting oxides using a simple thermolysis procedure. Photographs showing the phase-transferred Au–Pd and In–Sn/TOABr complexes.
shows the areal capacitance of the device calculated from the CV curves as a function of the scan rate. The highest specific capacitance of 75 F g\(^{-1}\) was achieved at the scan rate of 20 mV s\(^{-1}\), which decreases with increasing scan rates. It preserves nearly 40% of the initial capacitance when the scan rate increases from 20 to 100 mV s\(^{-1}\). The drop in the capacitance might be due to the mesoporous nature of Au−Pd electrodes providing a limited diffusion rate of electrolyte ions to form EDL across the interface. Galvanostatic CD curves were measured between 0 and 0.8 V potential window. As shown in Figure 3c, the CD curves are nearly triangular, which confirms the electrochemical double layer formation and efficient charge transfer across the Au−Pd electrodes. The stability of the device was illustrated by performing CD cycling for 200 times. As shown in Figure 3d, the device shows nearly 100% capacitance retention, and there was no change in the morphology of the electrode as well after 200 cycles (see the Supporting Information Figure S6).

The direct micromolding process involves a soft PDMS stamp as the mold, replica from the polycarbonate backing of the master (compact disc). The micromolding process described in this study consists of three steps mentioned in detail in the Experimental Section, and the schematic illustration is shown in Figure 4a. The obtained patterns are bearing a highly smooth surface without any cracks over large

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**Table 1. Details about Synthesis Procedures and the Obtained products**

| s.no. | M\(_1\)M\(_2\)−ToABr (M\(_1\)M\(_2\)) | thermolysis condition | end product | morphology | particle size | property | more details in figure |
|------|-------------------------------------|----------------------|------------|-------------|-------------|---------|----------------------|
| 1    | Au/Pd 1:1                          | 250 °C, 3 h, air     | bimetallic Au−Pd | particulates | 0.01−2 μm  | R < 10 Ω | 2, 4, S7             |
| 2    | Au/Pd 1:1                          | 500 °C, 3 h, air     | alloy Au\(_{0.52}\)−Pd\(_{0.48}\) | particulates | 0.01−2 μm  | ρ = 65.3 μΩ cm, supercapacitor, μ-grating | 2, 3, S1, S5, S6 |
| 3    | Au/Pt 1:1                          | 375 °C, 2 h, air     | bimetallic Au\(_{0.60}\)−Pt\(_{0.40}\) | particulates | 3−20 nm   | ρ = 73.0 μΩ cm, μ-grating | 4, S2, S5, S8 |
| 4    | Pt/Pd 1:1                          | 250 °C, 1 h, air     | alloy Pt\(_{0.55}\)−Pd\(_{0.45}\) | particulates | 10−100 nm | ρ = 86.6 μΩ cm, μ-grating | 4, S2, S3, S5 |
| 5    | Au/Cu 1:3                          | 375 °C, 3 h, N\(_2\) | alloy Au\(_{0.45}\)−Cu\(_{0.55}\) | plates      | 2−10 μm   | R < 3 Ω, μ-grating  | 4, S4    |
| 6    | Au/Cu 1:6                          | 375 °C, 3 h, N\(_2\) | alloy Au\(_{0.40}\)−Cu\(_{0.60}\) | plates      | 5−15 μm   | R < 3 Ω          | S4       |
| 7    | Au/Cu 1:9                          | 375 °C, 3 h, N\(_2\) | alloy Au\(_{0.45}\)−Cu\(_{0.55}\) | plates      | 1−5 μm    | R < 3 Ω          | S4       |
| 8    | In/Sn 5.2:1                        | 500 °C, 1 h, air     | ITO In\(_{0.9}\)Sn\(_{0.1}\)O\(_2\) | particulates | 100−300 nm | R\(_s\) ≈ 45 Ω/mm, T ≈ 77%, μ-grating | 5        |

ρ-resistivity, R-resistance, T-transmittance.
areas as evident from AFM and its height profiles, and SEM images of Au−Pd-1, Au−Pt, and Au−Cu-1 (Figures 4b−e and the Supporting Information S7 & S8). As revealed from the AFM height profile overlaid in Figure 4d, the Au−Pt \( \mu \)-strip possesses less surface roughness with a height of \( \sim 50 \) nm. Although Pt−Pd \( \mu \)-patterns were realized over several hundred microns (Figure 4f), unlike Au-based bimetals, Pt−Pd \( \mu \)-gratings are composed of large-sized nanoparticles, which are confirmed through AFM imaging (Figure 4g).

To prepare \( \sim 10\% \) Sn-doped indium oxide thin films with good conductivity through a wet chemical process, the In−Sn TOABr precursor was drop-coated on a glass substrate followed by thermolysis at 500 °C in air. By appropriately changing the ratio of tin and indium precursors, one can tune properties such as the morphology, electrical conductivity, and optical transparency of the obtained ITO film. The SEM image in Figure 5b shows the particulate nature of the film, which is further evident from the powder XRD pattern (Figure 5a). The sheet resistance of the ITO film is \( \sim 45 \Omega/\square \) with nearly 77% transmittance at 550 nm (Figure 5c). The partial loss of transmittance may have a contribution from the haze of the film and the substrate because of air reference. The haze values can be reduced by adopting the spray pyrolysis method instead of drop-coating. The sheet resistance of the obtained ITO film was lower than other wet chemical methods, even though the processing temperature was much less than the reported literature.21,36 As this organic precursor ink is easily amenable for direct micromolding, the ITO \( \mu \)-gratings were obtained over a large area. While patterning, the injected precursor decomposes in the microchannels of the PDMS stamp and leads to the closely packed fine ITO nanocrystals in the patterned stripes, mimicking the stamp geometry. Figure 5d shows the large area \( \mu \)-pattern of ITO on a silicon surface, and magnified views are shown in Figure 5e. The inset SEM image in Figure 5e and the AFM image (Figure 5f) depicts that ITO \( \mu \)-gratings are composed of fine nanoparticles. The patterning of ITO can be extended to other substrates such as mica, kapton, and so forth, which will offer flexibility as well as transparency for various optoelectronic applications.

It may be worthwhile to discuss the few merits of these M−TOABr precursors and their patternability. To prepare a metal−TOABr precursor, the formation of the complex between the metal anion and the TOABr is a crucial step, as it greatly affects the phase transfer efficiency of metal ions. As most of the metals form an anionic complex, it can readily form
a complex with TOABr and can be easily transferred to the organic medium. Unlike aqueous metal salt solutions, these M–TOABr precursors are easily processable as they form smooth films, important for creating high-resolution patterns. Unlike conventional lithographic methods, this direct patterning process using soft lithography does not use polymeric resists and is not a multistep process such as polymer exposure, development, and deposition of metal followed by lift-off. Instead, injecting the metal–TOABr precursor into the microchannels followed by thermolysis under a controlled atmosphere lead to desired μ-patterns of various bimetal and oxide combinations. Using the soft lithography process, here, we achieved the patterning over several hundred μm². Nevertheless, large-area parallel lithography techniques such as nanoimprinting could also be used for realizing the patternings over cm² areas with these metal–organic precursors as they are amenable for such processes. More importantly, these precursors are also compatible for the e-beam lithography process, as the precursor bearing long TOABr carbon chains undergoes chain cross-linking upon exposure to e-beam, and it allows the fabrication of nanopatterns of active materials.

CONCLUSIONS

In this study, thin films of various bimetals such as Au–Pd, Au–Pt, Au–Cu, Pt–Pd and transparent oxide such as ITO were synthesized using metal anion alkyl ammonium complex-based single-source precursors. The obtained films were characterized in detail and studied its electrochemical stability through the fabrication of the supercapacitor device. The μ-grating structures of bimetals and TCOs have been achieved using the process of micromolding in the capillary, employing patterned PDMS as the mold. The gratings of materials were realized by injecting the precursor into the microchannel created between the PDMS and the substrate followed by thermolysis at the prescribed atmosphere. This method can be adopted for micropatterning of many other metals or materials as the process is extremely viable but has a wide range of applications. Besides, nanopatterns of these materials could also be readily realized through the electron beam lithography process as the precursor is sensitive toward e-beam.

EXPERIMENTAL SECTION

Material and Methods. The metal precursors such as K₂PtCl₆, PdCl₂, In₂O₅, and SnCl₂·2H₂O were purchased from Sigma-Aldrich, whereas CuCl₂, HAuCl₄, tetraoctylammonium bromide (TOABr), and KOH from Spectrochem, India. They were used without further purification. Double-distilled and deionized water was used in this study. To 10 mL of 50 mM deionized water was added and stirred to aid the solution (phase transfer agent) was added and stirred to aid the transfer of metal ions (e.g., Cu, Sn, and In ions) to an organic medium. Unlike aqueous metal salt solutions, these precursors are easily processable as they form smooth films, important for creating high-resolution patterns. However, large-area parallel lithography techniques such as nanoimprinting could also be used for realizing the patternings over cm² areas with these metal–organic precursors as they are amenable for such processes. More importantly, these precursors are also compatible for the e-beam lithography process, as the precursor bearing long TOABr carbon chains undergoes chain cross-linking upon exposure to e-beam, and it allows the fabrication of nanopatterns of active materials.

Thick-Film Formation. The glass substrates (2 × 2 cm²) used for film formation were cleaned with soap water, deionized (DI) water, IPA, and acetone followed by drying under N₂ gas. A 200 μL of phase-transferred solution (i.e., Au–Pd/TOABr in toluene) was drop-coated over a glass substrate and annealed at an appropriate temperature on the hotplate/furnace with a high ramp rate.

Direct Micromolding. Glass and Si substrates were cleaned with DI water, acetone, and IPA solutions and dried under the N₂ atmosphere. An elastomeric PDMS stamp was obtained by mixing Sylgard 184 curing agent (Dow Corning) and its elastomer in the ratio of 1:10 thoroughly. After degassing the mixture under vacuum for 30 min, PDMS was coated onto the precleaned polycarbonate backing of the master (CD) and then cured at 90 °C for 5 h. The stamp peeled off from the master-contained protruding line feature of ∼505 nm width separated by ∼950 nm channels. The thickness of the stamp was ∼3 mm. The stamp was cleaned with hexane and ethanol subsequently to remove any uncured or low molecular mass oligomers and dried in the N₂ atmosphere. The micromolding process begins with (i) placing the precleaned and dried PDMS stamp over a clean substrate and (ii) injecting a molecular precursor followed by annealing and (iii) removing the stamp. Typically, the precursor solution of ∼60 μL (metal–TOABr complex) was injected from one end on a Si/glass substrate, on which a patterned PDMS was kept. When the PDMS stamp was pressed against the Si/glass substrate, it was sealed well such that only the microchannels are available for the precursors to flow because of capillary force (see schematic 4a). To further ensure the sealing, we have applied small pressures over the stamp by placing weights on top of the stamp. The temperature was slowly raised to 250 °C at the ramp rate of 1 °C min⁻¹ and dwelled at that temperature for 30 min (in the same controlled atmosphere mentioned for thin films). After cooling down to room temperature, the stamp was removed to realize the periodic lines of bimetals. For alloys and ITO gratings, the samples were further annealed at the prescribed temperature and atmosphere mentioned in Table 1. It must be noted that annealing at this stage does not widen the lines.

Electrochemical Measurements. The electrochemical properties of the fabricated bimetallic film (Au–Pd-2) were investigated in the two-electrode configuration using a 6 M KOH aqueous electrolyte. Whatman filter paper (pore size of 220 nm) was used as a separator between two bimetallic electrodes. CV and galvanostatic CD measurements were performed using the potentiostat equipment from Tecnoscientific Instruments (model PG16250). The specific capacitance values are calculated using the equation \( C_{\text{sp}} = \frac{2}{m_i(1/s)} \) where \( m_i \) is the total mass of the electrodes, \( I \) is the current in mA, and \( s \) is the sweep rate in mV s⁻¹.

Characterization. XRD measurements were performed using a Siemens Seifert 3000TT diffractometer (Cu Kα 1.5406 Å, scan rate, 0.5 min⁻¹). The EDS mapping was performed at 10 kV (energy window, 10 eV) with a beam current of 1.1 nA, the dwell time per pixel is 30 s in the Nova NanoSEM 600 instrument (FEI Co., The Netherlands). TEM was performed in the JEOL-3010 instrument. AFM images were taken using a Digital Instruments Multimode head attached to a Nanoscope-IV controller (Veeco, USA). UV–visible spectrum was recorded using a PerkinElmer Lambda 900 UV/vis/near-IR spectrophotometer.
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TEM and ED pattern of Au–Pd; XRD, SEM, and TEM images of Pt–Pd and Au–Pt bimetal; SEM images of Pt–Pd thin films; XRD and SEM of various Au–Cu alloy compositions; comparison of resistivity of various bimetal thin films; stability of the Au–Pd electrode after supercapacitor testing; 3D AFM view of Au–Pd μ-stripes; and optical micrograph and SEM image of the Au–Pt μ-stripes (PDF)

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**Author Contributions**

S.K. and B.R. designed and directed the project, performed the experiments. B.R. and S.K. synthesized the precursor inks. S.K. performed electrochemical measurements and analyzed the results. S.K. and B.R. wrote the manuscript and have given the approval to the final form.

**Notes**

The authors declare no competing financial interest.

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