

## Growth of anisotropic gold nanostructures on conducting glass surfaces

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**Abstract.** In this paper, we describe a method for the growth of gold nanowires and nanoplates starting from a bilayer array of gold seeds, anchored on electrically conducting indium tin oxide (ITO) substrates. This is based on a seed-mediated growth approach, where the nanoparticles attached on the substrate through molecular linkages are converted to nanowires and nanoplates at certain cetyltrimethylammonium bromide (CTAB) concentration. Our modified approach can be used to make nanowires of several tens of micrometers length at a lower CTAB concentration of 0.1 M. The length of the nanowires can be varied by adjusting the time of the reaction. As the concentration of CTAB was increased to 0.25 M, the nanoparticles got converted to nanoplates. These Au nanoplates are (111) oriented and are aligned parallel to the substrate.

**Keywords.** Gold; ITO; nanowires; nanoplates; seed-mediated growth.

### 1. Introduction

Synthesis of metal nanoparticles of diverse shape and size has become a major area of research due to their geometry-dependent properties and potential applications in chemical<sup>1</sup>/optical sensing,<sup>2</sup> nanoelectronics,<sup>3</sup> surface enhanced Raman scattering (SERS),<sup>4</sup> metal enhanced fluorescence<sup>5</sup> and catalysis.<sup>6</sup> Heterostructure assembly of such hybrid wires exhibits exceptional electron transfer properties.<sup>7</sup> Several synthetic approaches such as photochemical,<sup>8</sup> biological,<sup>9</sup> templated,<sup>10</sup> electrochemical<sup>11</sup> and surfactant-based seed-mediated<sup>12</sup> growth methods have been reported for making anisotropic nanostructures of gold and silver. In order to fabricate functional materials and devices, it is necessary to have an assembly of these nanoparticles onto solid planar substrates. For this, one can use sophisticated methods such as nanosphere lithography.<sup>13</sup> Several other methods are also employed for the fabrication of one-dimensional (1D) and two-dimensional (2D) nanostructures on planar surfaces such as seed mediation,<sup>14</sup> immobilization of nanostructures onto self-assembled monolayers (SAMs) via covalent interactions,<sup>15</sup> growth of anisotropic nanostructures along the direction of gas flow,<sup>16</sup> electrochemical deposi-

tion,<sup>17</sup> galvanic displacement reactions,<sup>18</sup> sputter deposition and thermal vapor deposition.<sup>19</sup> We have explored several possibilities of immobilized metal nanoparticle assemblies on planar surfaces in order to make sensors and devices.<sup>20,21</sup> At present, the fabrication of uniform anisotropic metal nanostructures like Au plates and wires with high yield and well-defined morphologies is still a challenge.

Our research group is actively engaged in the synthesis, characterization and application of various anisotropic metal nanostructures. We developed a methodology to fabricate aligned array of equilateral gold nanotriangles on ITO substrate via a potential assisted seed-mediated approach.<sup>22</sup> This substrate showed an intense near infrared (NIR) absorption and strong surface enhanced Raman activity. We have recently reported the cupric ion assisted shape transformation of AuNRs into spherical AuNPs.<sup>23</sup> The intermediate structures formed during this shape transformation could be arrested at any stage to produce nanoparticles of preferred shape. Here, selective etching of the tips of the nanorods occurs at higher concentration of CTAB and subsequent shape transformation is driven by the surface reconstruction of nanorods to produce more stable planes. A solution phase method for assembling gold nanorod-coated poly(*N*-isopropyl acrylamide) microgels into a hexagonal pattern was reported recently from our group.<sup>24</sup> These patterns were made by growing the

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seed nanoparticle attached to the microgels into nanorods.

In this paper, we report a method for the growth of 1D and 2D nanostructures of gold such as nanowires and nanoplates on ITO surfaces by a seed-mediated growth method. Several such seed-mediated processes have been reported in the recent past, especially for anisotropic nanostructures such as nanorods. The method reported here is an adaptation of the seed mediated growth of gold nanorods on mica surfaces reported by Taub *et al.*<sup>25</sup> Our method enables the control of size and shape of the nanostructures on ITO by varying the experimental parameters such as the growth time, concentration of surfactant and temperature of the reaction.

## 2. Experimental

### 2.1 Materials

Tetrachloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), CTAB, sodium citrate and ascorbic acid (AA) were purchased from CDH, India. Sodium borohydride ( $\text{NaBH}_4$ ), 1,9-nonanedithiol (NDT) and aminopropyltrimethoxysilane (APTMS) were purchased from Aldrich. ITO with a resistivity of  $70 \Omega/\text{cm}$  was used

throughout this work. All chemicals were used as such without further purification. Triply distilled water was used throughout the experiments.

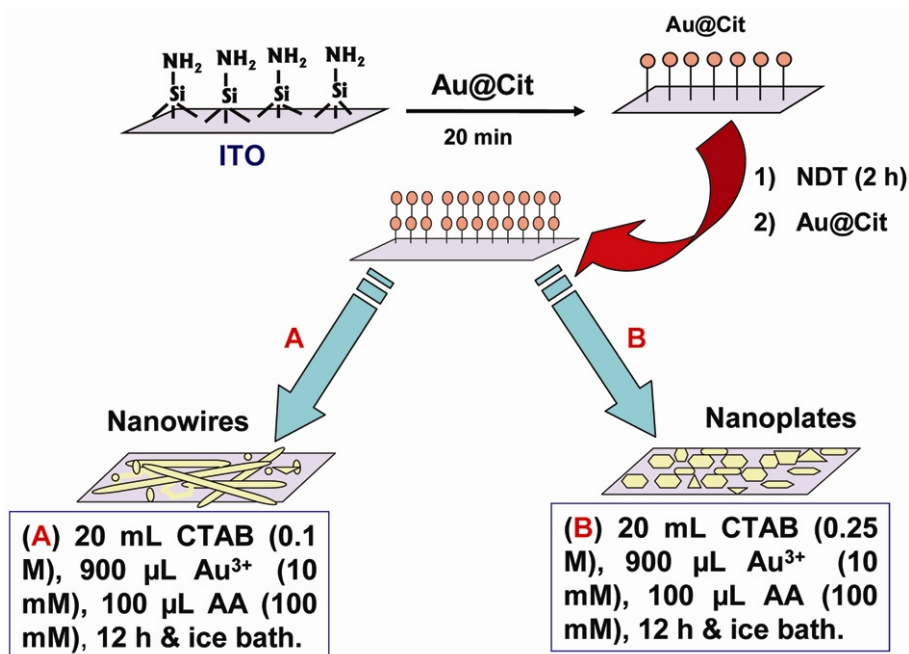
Scheme 1 shows the experimental procedure employed for making nanowires and nanoplates on ITO substrate.

### 2.2 Preparation of ITO substrates

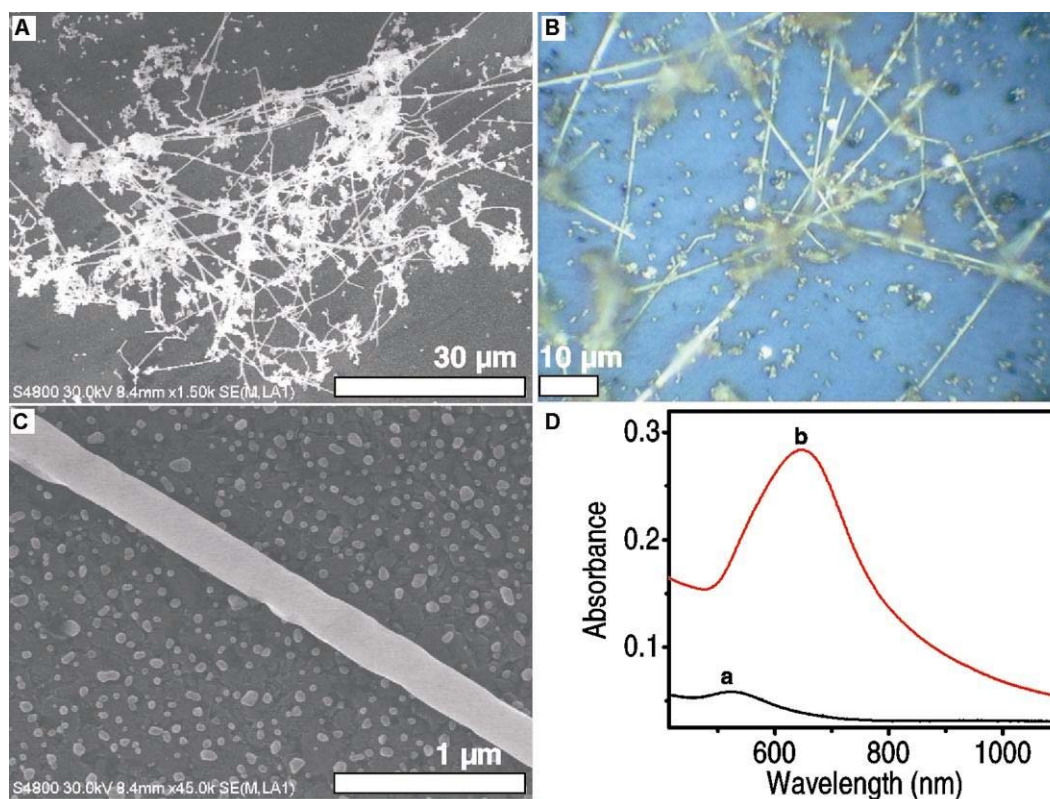
The ITO glass slides of dimensions  $1 \text{ cm} \times 2 \text{ cm}$  were sonicated with a mild detergent solution, ethanol and finally with pure water (in the order mentioned). They were then soaked in a 10% HCl solution for activation, washed with water, and dried under a stream of nitrogen. These plates were annealed at  $450^\circ\text{C}$  for 7 h and cooled in a desiccator. The glass slides were dipped in 30 mM APTMS solution in methanol for 1 h. Afterwards, they were washed with methanol and water in sequence and kept at  $100^\circ\text{C}$  for 2 h.

### 2.3 Preparation of gold seed

4 to 8 nm diameter AuNP seeds were synthesized by taking 37 mL of water in a beaker and 1 mL, 0.01 M  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and 1 mL, 0.01 M aqueous trisodium-



**Scheme 1.** Procedure for the growth of gold nanoplates and nanowires on ITO substrates.



**Figure 1.** (A) SEM image of gold nanowires formed on ITO after 12 h of the reaction; (B) optical image of the nanowires formed after 12 h of reaction; (C) SEM image of an enlarged portion of a single gold nanowire and (D) UV-vis spectra of the nanoparticle coated ITO (a) and the nanowires formed (b).

citrate solution was added to it. Then 1 mL of ice cold solution of 0.1 M aqueous  $\text{NaBH}_4$  was added and the solution was stirred for 5 min.

#### 2.4 Growth of gold nanowires on ITO substrates

The APTMS coated ITO substrate was immersed in the seed solution for a period of 20 min. The substrate was washed with water and dried. This substrate was then dipped in a 30 mM solution of NDT in methanol for 2 h. Subsequently, this substrate was dipped in the nanoparticle solution (20 min) again, in order to get a bilayer assembly of nanoparticles.

The bilayer of seed coated ITO substrate was then immersed in 20 mL, 0.1 M CTAB solution for 3 min. After this 900  $\mu\text{L}$ , 0.01 M  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was added followed by 100  $\mu\text{L}$ , 0.1 M ascorbic acid. This growth vessel was kept inside an ice bath throughout the process and allowed to stand undisturbed for 12 h. The nanowire formation was evident by the colour change of the ITO substrate from colourless to sand-like appearance. In order to get nanowires of various lengths, we changed the reaction time. It was noted

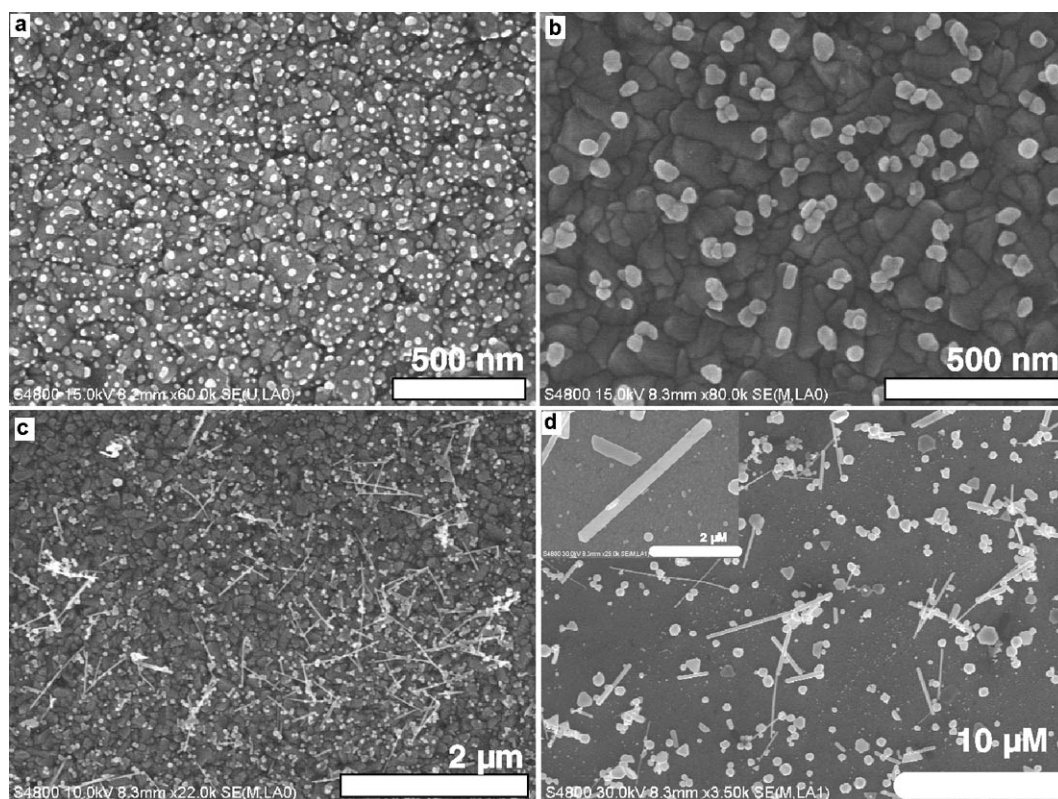
that as the reaction time increases, the length of the nanowires was increased. After the completion of the growth, the substrate was taken out, washed using distilled water in order to remove the excess CTAB and was characterized.

#### 2.5 Growth of gold nanoplates on ITO substrates

The bilayer of seed coated ITO substrate was immersed in 20 mL, 0.25 M CTAB solution for 3 min. After this, 900  $\mu\text{L}$ , 0.01 M  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was added followed by 100  $\mu\text{L}$ , 0.1 M ascorbic acid. This growth vessel was kept inside an ice bath throughout the process and allowed to stand undisturbed for 12 h. The nanoplate formation was evident by the colour change of the ITO substrate from colourless to pale pink.

#### 2.6 Instrumentation

Scanning electron microscopic (SEM) and energy dispersive analysis of X-rays (EDAX) studies were



**Figure 2.** SEM images showing the gold nanowires formed at different time intervals (a) 15 min, (b) 30 min, (c) 4 h and (d) 8 h. Inset shows the SEM image of a single nanowire formed after 8 h.

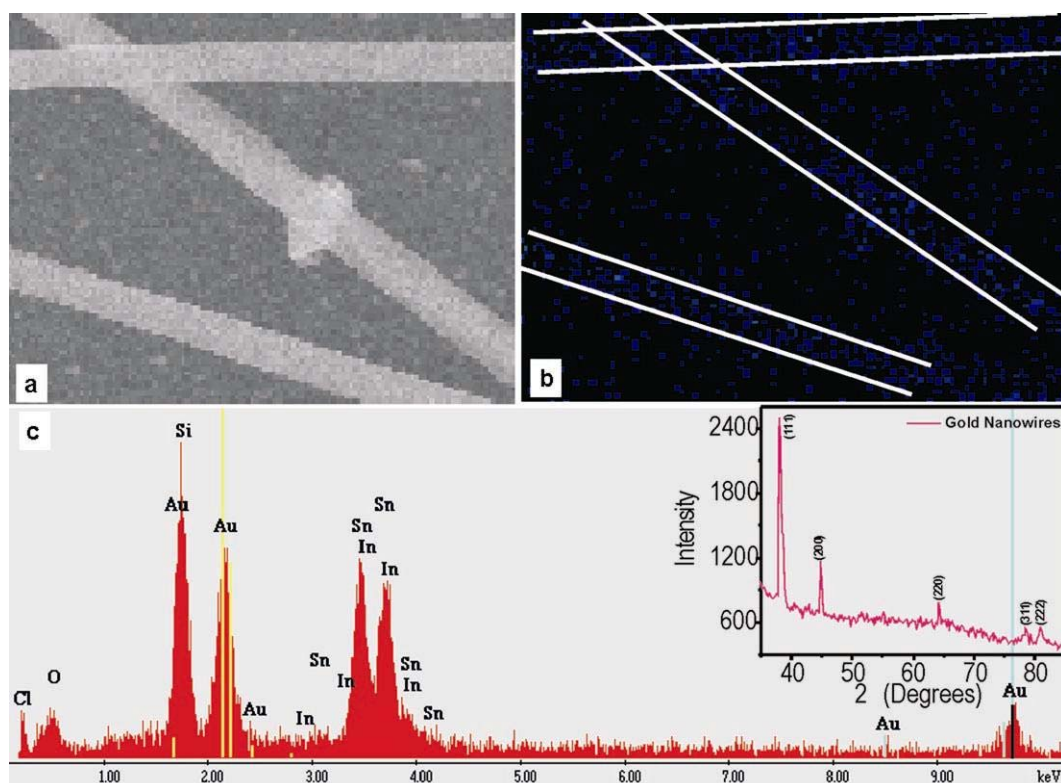
done in a HITACHI S-4800 FE-SEM. UV-vis spectra were measured using a Perkin–Elmer Lambda 25 spectrometer. Optical images were taken using a WiTec GmbH, Alpha-SNOM CRM 200 spectrometer. X-ray diffraction (XRD) data were collected with a Shimadzu XD-D1 diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The samples were scanned in the  $2\theta$  range of 10–90 degrees.

### 3. Results and discussion

The gold nanowires and nanoplates were grown on ITO substrate via a modified seed-mediated growth method. The characterization of these nanostructures was done by optical absorption measurements, SEM and XRD. We succeeded to tune the length of nanowires ranging from few nanometres to several tens of micrometers. Figure 1A shows a large area SEM image of the gold nanowires formed after 12 h of reaction. It is clear from the image that a large number of nanowires were formed and most of the nanowires have more than  $100 \mu\text{m}$  length. These nanowires were also visible under the optical micro-

scope. Figure 1B shows an optical microgram of the nanowires grown under similar conditions. Figure 1C shows an enlarged portion of a single nanowire. The diameter of these nanowires is in the range of  $\sim 100 \text{ nm}$ . UV-vis spectra of nanoparticle-coated ITO and nanowires formed after 12 h of the reaction are shown in figure 1D. The UV-vis spectrum of the AuNPs coated ITO exhibited an absorption maximum at 520 nm, which is due to the surface plasmon resonance (SPR) of spherical gold nanoparticles. After the reaction, the SPR band of nanoparticle coated ITO red shifted to 650 nm indicating the growth of nanowires. The background of the absorption spectrum slightly increased after the reaction indicating the formation of large anisotropic nanostructures.

The length of the nanowires can be tuned by varying the reaction time. As the time of reaction increases, the length of the nanowires was found to be increased. One of the advantages of our synthetic approach over the other seed-mediated growth methods reported earlier is that we can make nanowires of length larger than  $100 \mu\text{m}$ . Such nanowires would be useful for making conductive components in



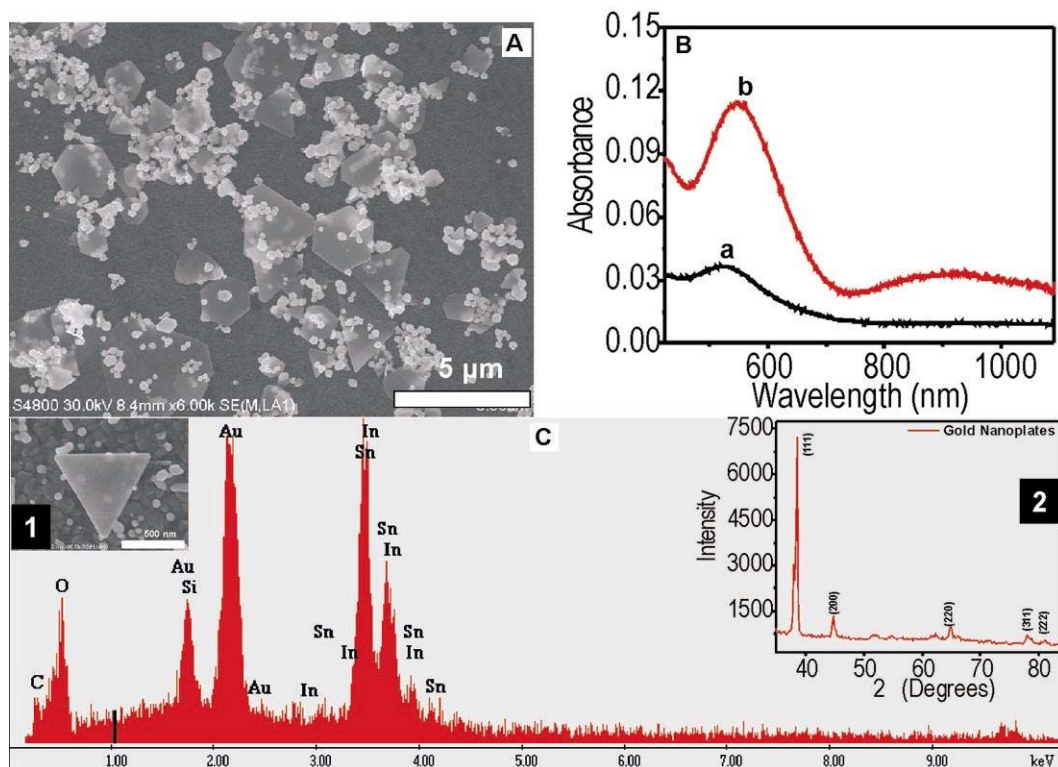
**Figure 3.** (a) SEM image of the nanowires formed on ITO after 12 h; (b) EDAX mapping of Au nanowires shown in a and (c) EDAX spectrum of a gold nanowire. Inset of c shows an XRD pattern of the nanowires formed after 12 h of the reaction.

electronics. We can make nanowires of desirable length by stopping the growth at various stages of the reaction. Figures 2a–d show the nanowires formed at various time intervals such as 15 min, 30 min, 4 h and 8 h of the reaction, respectively. After 30 min of the reaction, the nanoparticles grown on the substrate were smaller rods of  $\sim 100$  nm length. After 4 h of the reaction, the length of most of the nanowires were 1 to 2  $\mu\text{m}$ . Inset of figure 2d shows the SEM image of a single nanowire formed after 8 h of the reaction.

The nanowire growth happens from the multiply twinned seed nanoparticles by the passivation of certain crystallographic planes of the Au seed by the adsorption of CTAB. This results in the growth of anisotropic particles. The CTAB forms a bilayer which stabilizes and retards the growth along Au (110) face of the nanorods and promotes the growth at the tip.<sup>26</sup> Low temperature enhances the growth rate. It is noticed that the bilayer of nanoparticles immobilized on the ITO results in the formation of much lengthy nanowires compared to a monolayer of nanoparticles. In the case of a monolayer of nanoparticles, the maximum length of the nanowires was found to be less than 5  $\mu\text{m}$ . Figure 3a shows a magnified SEM

image of nanowires grown on ITO after 12 h of reaction and corresponding EDAX mapping of Au of these nanowires is shown in figure 3b. An EDAX map and the spectrum taken from the nanowires confirm that these nanostructures are made of gold. This is further confirmed by XRD. Inset of figure 3c shows the XRD of the as prepared nanowires coated ITO substrate. The XRD patterns of the nanowires were assigned to the (111), (200), (220), (311) and (222) reflections of face-centered cubic gold.

In the seed-mediated growth approach, the concentration of the surfactant plays an important role in the morphology determination. Mirkin *et al.*<sup>27</sup> synthesized nanotriangles starting from 4 nm Au@Citrate seed nanoparticles using a growth solution containing saturated CTAB. In order to grow nanoplates on the ITO substrate, we increased the concentration of CTAB and kept all other parameters constant. We used 0.25 M of CTAB. In the case of nanowire growth, it was 0.1 M. A typical large area SEM image of the gold nanoplates grown on ITO substrate at this condition after 12 h of reaction is shown in figure 4A. These nanoplates have smooth



**Figure 4.** (A) SEM image of the gold nanoplates formed on ITO after 12 h of the reaction; (B) UV-vis spectra of (a) nanoparticle coated ITO and (b) nanoplates formed under the same condition and (C) EDAX spectrum taken from the nanoplate shown in inset 1. Inset 2 shows the XRD of the nanoplates formed under the same condition.

surfaces and have a thickness less than 50 nm. With this procedure, nanoplates with an edge length from 1 to 3  $\mu\text{m}$  were formed on the ITO surface. These nanostructures contain hexagonal shaped nanoplates, nanotriangles and truncated triangular nanoplates. Figure 4B shows the absorption spectra of nanoparticle coated ITO and nanoplates formed after 12 h. The absorption spectrum of the nanoparticle coated ITO shows a single absorption maximum at 520 nm and there was no absorption observed at longer wavelength. As the growth proceeds, the SPR of the nanoparticle centered at 520 nm red shifted to 550 nm and a broad absorption band appeared in the NIR region indicating the formation of gold nanoplates. The broad peak in the NIR region is attributed to in-plane SPR of nanoplates and that observed at 550 nm is due to their out of plane SPR.<sup>27</sup>

The intensity ratio of the (111) and (200) diffraction peaks in the XRD pattern (inset 2 of figure 4C) of nanoplates was higher than the bulk value. This result suggests that the Au nanoplates were rich in (111) planes and their (111) planes are preferentially

oriented parallel to the surface of the ITO substrate. The EDAX spectrum (figure 4C) taken from a single nanoplate (inset 1) confirms that these nanoplates are made of gold. The dramatic change in the morphology is mainly attributed to the adsorption of CTAB on low index planes of gold. The growth solution contains CTAB in much higher concentration (0.25 M) which suppresses the overall crystal growth through specific adsorption on certain planes. This favours the formation of (111) oriented nanoplates. Low temperature favours the slow growth of the nanoparticles into nanoplates. It was noted that the bilayer of nanoparticle also has some influence on the formation of nanoplates. At the same condition, monolayers of nanoparticle were grown into bigger nanoparticles of irregular geometry.

#### 4. Conclusion

In conclusion, this paper describes a simple method to grow Au nanowires of length greater than 100  $\mu\text{m}$  and nanoplates of edge length 1–3  $\mu\text{m}$  on ITO sub-

strates via a modified seed-mediated growth approach. These nanostructures were grown on an ITO substrate covered with a bilayer of Au nanoparticles. The length of the nanowire can be varied by adjusting the time of the reaction. It was found that the concentration of CTAB and temperature play an important roles in the morphology determination. The products were characterized by UV-vis spectroscopy, SEM, XRD and optical microscopy. These nanostructures could have promising applications in surface enhancement spectroscopic methods.

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### References

- Haes A J, Hall W P, Chang L, Klein W L and Van Duyne R P 2004 *Nano Lett.* **4** 1029
- Haes A J and Van Duyne R P 2002 *J. Am. Chem. Soc.* **124** 10596
- (a) Kovtyukhova N I, Martin B R, Mbindyo J K N, Smith P A, Razavi B, Mayer T S and Mallouk T E 2001 *J. Phys. Chem.* **B105** 8762; (b) Sun S H, Murray C B, Weller D, Folks L and Moser A 2000 *Science* **287** 1989
- (a) Champion A and Kambhampati P 1998 *Chem. Soc. Rev.* **27** 241; (b) Tian Z, Ren B and Wu D 2002 *J. Phys. Chem.* **B106** 9463
- Aslan K, Lakowicz J R and Geddes C D 2005 *J. Phys. Chem.* **B109** 6247
- Street S C, Xu C and Goodman D W 1997 *Annu. Rev. Phys. Chem.* **48** 43
- Sharma J, Vivek J P, Vijayamohan K P, Singh P and Dharmadhikari C V 2006 *Appl. Phys. Lett.* **88** 193103
- (a) Maillard M, Huang P and Brus L 2003 *Nano Lett.* **3** 1611; (b) Jin R, Cao Y, Mirkin C A, Kelly K L, Schatz G C and Zheng J G 2001 *Science* **294** 1901
- Shankar S S, Rai A, Ankamwar B, Singh A, Ahmad A and Sastry M 2004 *Nat. Mater.* **3** 482
- (a) Hong B H, Bae S C, Lee C W, Jeong S and Kim K S 2001 *Science* **294** 348; (b) Zong R L, Zhou J, Li Q, Du B, Li B, Fu M, Qi X W, Li L T and Buddhudu S 2004 *J. Phys. Chem.* **B108** 16713; (c) Adhyapak P V, Karandikar P, Vijayamohan K, Athawale A A and Chandwadkar A J 2004 *Mater. Lett.* **58** 168
- Yu Y Y, Chang S S, Lee C L and Chris Wang C R 1997 *J. Phys. Chem.* **B101** 6661
- Busbee B, Obare S and Murphy C J 2003 *Adv. Mater.* **15** 414
- Haynes C L and Van Duyne R P 2003 *Nano Lett.* **3** 939
- Umar A A and Oyama M 2006 *Cryst. Growth Des.* **6** 818
- Gole A, Orendorff C J and Murphy C J 2004 *Langmuir* **20** 7117
- Huang S, Cai X and Liu J 2003 *J. Am. Chem. Soc.* **125** 5636
- (a) Notsu H, Kubo W, Shitanda I and Tatsuma T 2005 *J. Mater. Chem.* **15** 1; (b) Tian Y, Liu H, Zhao G and Tatsuma T 2006 *J. Phys. Chem.* **B110** 23478
- Wiederrecht G P and Sun Y 2007 *Small* **3** 1964
- Jia D and Goonewardene A 2006 *Appl. Phys. Lett.* **88** 53105
- Subramaniam C, Pradeep T and Chakrabarti J 2005 *Phys. Rev. Lett.* **95** 164501
- Subramaniam C, Pradeep T and Chakrabarti J 2007 *J. Phys. Chem.* **C111** 19103
- Sajanlal P R and Pradeep T *Adv. Mater.* (in press)
- Sreeprasad T S, Samal A K and Pradeep T 2007 *Langmuir* **23** 9463
- Rajeev Kumar V R, Samal A K, Sreeprasad T S and Pradeep T 2007 *Langmuir* **23** 8667
- Taub N, Krichevski O and Markovich G 2003 *J. Phys. Chem.* **B107** 11579
- Wei Z and Zamborini F P 2004 *Langmuir* **20** 11301
- Millstone J E, Park S, Shuford K L, Qin L, Schatz G C and Mirkin C A 2005 *J. Am. Chem. Soc.* **127** 5312