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Gold nanorod libraries enhancement for optical imaging

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ABSTRACT

Efficient far-field coupling of longitudinal plasmon modes of gold nanorods makes them prospective for optical imaging. A facile one-step hydrothermal synthesis of stabilized gold nanorods in an aqueous solution at 85 °C is reported. High aspect ratio of these nanorods ranging from 10 to 57 is achieved using methyltrioctylammonium chloride (TOMAC) as a phase transfer reagent. The growth of {100} and {110} facets being more favorable to conception is facilitated via the capping agent (TOMAC). These highly elongated nanorods reveal visible luminescence at around 410 nm, which is attributed to the ligand–metal charge transition mechanism. We affirm that such plasmonic nanorods acquiring superior nonlinear optical properties can be used as a vehicle for single-particle measurements.

1. Introduction

Anisotropic Au nanorods (NRs) owing to their aspect ratio mediated superior optical features are advantageous for optical imaging/sensing [1–3]. The preparation of Au NRs traditionally involves a seed-mediated growth mechanism in the presence of a cationic quaternary ammonium salt (hexadecyltrimethylammonium bromide/CTAB) as a shape directing and capping agent [4] and has been reported many times. This seed-growth approach can produce Au NRs with aspect ratios (length/diameter) as much as 27:1. However, the growth conditions control usually offers complexes [5] with another limitation related to its aspect ratio reduction with the growth progression [6]. Thus, an alternative synthesis method is required to achieve dispersed and elongated Au NRs with localized surface plasmon resonance (LSPR) effects in the IR region.

The surface ligand and aspect ratio of Au NRs are prerequisite for near-field optical response [7]. Usually, NRs aspect ratio is directing surfactant's nature dependent (in an aqueous solution) [8] and a surfactant's (CTAB) concentrated solution is necessary. CTAB binds to the surface of Au as bilayer structure and has limitations in terms of its toxicity and stability [9,10]. Often, $AgNO_3$ is used as additive for selective binding and packing of CTAB but it reduces the repulsion between the surfactant headgroups [11]. Despite this additive, preparation of NRs with aspect ratio >7 becomes difficult [12]. Many experiments exhibited the effect of alkyltrimethylammonium (surfactant) tail length [8] and surfactant's head group [13] on Au NRs growth.

TOMAC/Aliquat 336 is another cationic quaternary ammonium liquid surfactant and ordinarily employed metal extraction reagent. It is more stable against air and moisture attack than other cationic ligands and easy to handle [14]. This strong surfactant is partially soluble in water [15] which causes TOMAC molecular leakage into colloidal solution substantially lower than usual CTAB/CTAC surfactants. The change of Au NRs morphology (aspect ratio) via different synthesis temperature programs are reported [16], but the impact of reaction time duration is not yet documented. We prepare Au NRs of very high aspect ratio (ranging from 10 to 57) in an aqueous solution at 85 °C using TOMAC as a phase transfer reagent. The effects of TOMAC concentration, reaction temperature and time on the structure, optical behavior, and product yield are determined.

2. Experimental

Au NRs are prepared using the modified literature protocol [17], where 0.058 g of TOMAC (Sigma Aldrich, 88.2–90.6%) is dissolved in deionized water (9.3 mL) and stirred for 30 min to form micelles. Then, 500 μL of 10 mM hydrochloroauric acid/$HAuCl_4$

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(Sigma Aldrich, 99.999%) and 200 μL of 0.05 M anhydrous trisodium citrate/$Na_3C_6H_5O_7$ (Merk, 94–100.5%) are added to TOMAC solution and heated at 85 °C for 24 h. Finally, the obtained brownish purple solution containing high aspect ratio Au NRs is washed with deionized water while centrifuging three times at 800 rpm for 15 min each. The characterization detail is provided in Supporting information.

3. Results and discussion

For the first time, we report the one-step hydrothermal synthesis of very high aspect ratio Au NRs using TOMAC as a capping agent. Fig. 1(a) shows the EDX spectrum and (b–i) shows the TEM images of as synthesized Au NRs. Most of them are highly mono-dispersed because the yield drops off steeply as the aspect ratio increases above 4:1 [18] and few appear in the bunch including some hexagonal or pruned triangular shapes. Longer NRs revealed narrower widths and high anisotropy, whereas wire-liked NRs possessed bending ability with much tolerance. As surface energies of larger NPs are lower than those of smaller ones, smaller NPs are consumed with increasing the reaction time and then more stable NRs and nanowires (NWs) are formed (Table T1/Supporting information).

The processing parameters dependent alteration of nanostructures (NSs) shapes are enlisted in Table T1/SI where TOMAC contents are also found to influence strongly the NSs product yield (see Supporting information). Fig. 2(a) shows the UV–vis spectra of all samples. The splitting of the absorption peak (at 534 nm and 582 nm) for Sample 3 is ascribed to the presence of NCs along with some NTs of varying sizes. Sample 2 being a mixture of wire-like rods, NTs and NCs revealed a broad absorption peak around 550–650 nm. Conversely, the observed absorption band broadening until infrared region for Sample 1 is attributed to the extreme elongation of Au NRs. Furthermore, the shrinkage in NRs width indeed manifested a hypsochromatic (blue) shift of transverse palsmonic band accompanied by a small absorption at 470 nm. The decrease in intensity of the absorbance peaks of both transverse and longitudinal plasmonic bands are due to extreme enhancement in aspect ratio, low product yield and coupling effect [19]. Fig. 2(b) displays the shape distribution in Sample 1 where Au NRs with 60.53% yield are achieved and increased to 72% if we exclude nanoparticles as an intermediate product. Fig. 2(c) depicts the length distribution of Au NRs in Sample 1. In Fig. 2(d) the XRD pattern of Sample 1 shows primarily the (111) Bragg reflection of fcc gold nanocrystals at $2\theta = 38.81°$ in consistent with (JCPDS 04-0784), indicating highly oriented growth of the Au NRs. Notably the other Bragg reflections are extremely weak.

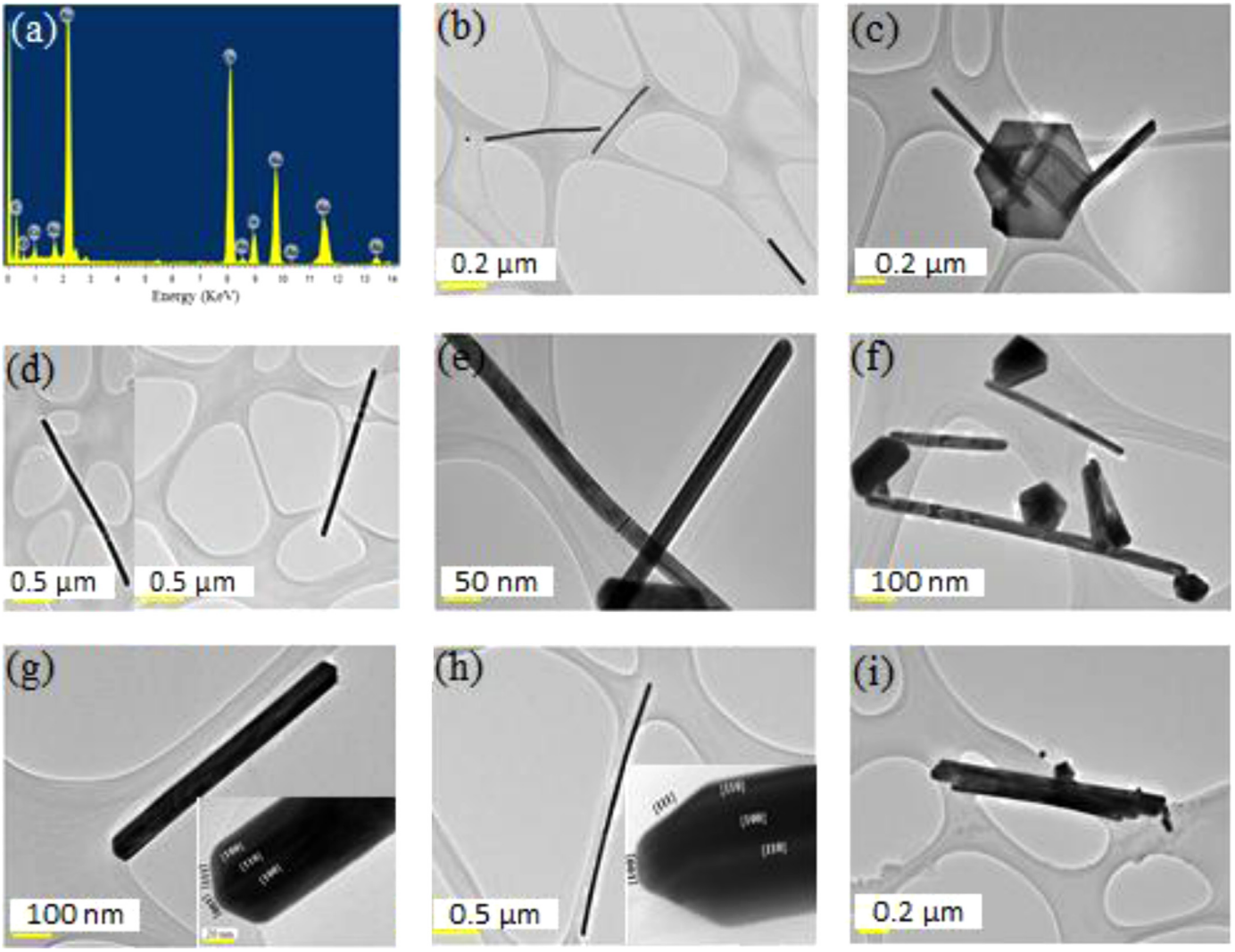

Fig. 1. (a) EDX spectrum of Au NRs (sample 1) and (b–i) TEM images of as synthesized Au NRs. Most of them are mono-dispersed (b,d,g,h) and few are in the bunch (f,i). The insets in (g) and (h) show HR-TEM images of octagonal Au NRs.