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Application of oil-swollen surfactant gels as a growth medium for metal nanoparticle synthesis, and as an exfoliation medium for preparation of graphene

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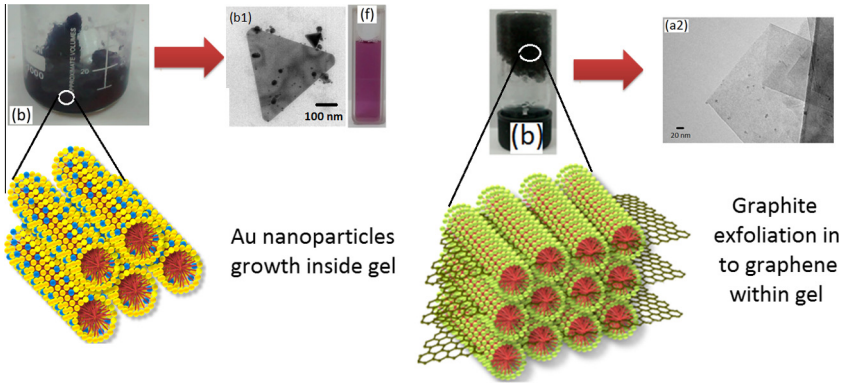
GRAPHICAL ABSTRACT



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ABSTRACT

Gel is an intermediate phase of solid and liquid, which exhibits properties of both, and this unique feature of gel has made it an excellent choice as a reaction medium for the nanomaterials synthesis. Herein, we report use of oil swollen surfactant gels as reaction medium and exfoliation medium, for the synthesis of metals (Au, Ag) nanoparticles and graphene, respectively. Confined growth of metals (Au and Ag) nanoparticles, has been achieved by exploring tween 80 based surfactant gel as a reaction medium. Au NPs prepared within tween 80 gel were found to be spherical with size ~5 nm, arranged in template micelles. Heating triggered the growth of Au nanoparticles and particles of various shapes including triangles, rods and pentagonal, were produced. Au and Ag containing tween 80 gels were found to be promising as catalysts for the nitrophenol reduction. Apart from separate synthesis of Au and Ag nanoparticles, bimetallic (Au-Ag) nanoparticles have also been synthesized by taking advantage of selective reducing property of tween 80. First time CTAB gel has been utilized as an exfoliation medium for the quick exfoliation of graphite into graphene sheets, eliminating the necessity of any external driving force such as sonication or heating, to reinforce exfoliation.

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1. Introduction

Owe to availability of wide application spectrum and ease of fabrication, surfactant self assemblies always remain a topic of interest among scientific communities. Out of myriad of applications credited to these self-organized surfactant arrays, use of these as templates, building blocks and stabilizing agents for the fabrication of nanomaterials, is highly studied [1–3]. Particularly, surfactant mesophases fabricated using judicially controlled conditions, have garnered huge attention as building molds for the growth of nanomaterials with diverse morphologies [4–7]. Surfactant mesophases offer several advantages as building blocks for the nanomaterials synthesis such as ease of fabrication, cost effective and highly rigid gel like structure of these mesophases endows strict control over the particle growth. Additionally, presence of rod shaped microstructure can facilitate one dimensional growth of the nanoparticles and thus can be useful for the preparation of nanowires [8–11] and nanotubes [12]. Surfactant mesophases have been widely explored as 'nanoreactors' [13] for the constrained growth of metal nanoparticles, particularly, for the Pd and Pt nanoparticles (NPs) these surfactant assemblies have been proven to be highly efficient. In the past decade, an omnibus of reports has been documented stating use of sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) based oil swollen liquid crystals as a reaction medium for the fabrication of various shapes of Pd and Pt NPs [4,14].

Graphene has garnered huge attention among scientific communities owe to its innumerable unprecedented properties, which have been extensively explored in several areas. A large number of fabrication approaches including mechanical exfoliation, chemical vapor deposition, chemical reduction and sono-chemical exfoliation, have been employed in order to obtain graphene. Each synthesis approach has its own merit, such as mechanical exfoliation is easy to execute and chemical reduction produces graphene, which can be easily dispersed in solvents to make suspensions. Out of abovementioned fabrication approaches, exfoliation is one of the highly practiced methods since it produces graphene with fewer defects. Exfoliation of graphite into graphene has been achieved through mechanical force, chemicals and sonication. Chemical assisted exfoliation produces graphene suitable for the wet chemical processing and also endows it flexibility of use in either solid or liquid suspension form, which expands its application domain [15]. Out of several chemicals, surfactants are in particular of great interest as exfoliating agents [16] since these amphiphilic molecules usually exhibit a long hydrophobic chain, which can interact non-covalently with the individual graphene sheets having likewise nature. Plethora of reports proclaiming surfactant assisted exfoliation of graphite have been appeared recently, however most of the reported exfoliation methods are lengthy and require significant amount of time to attain complete exfoliation of graphite, which is one of the shortcomings with these methods and need to be addressed in order to realize up scaling of exfoliation based graphene production. Apart from prolong processing time, use of additional driving forces such as heating, sonication and centrifugation to facilitate exfoliation, are another cost enhancing elements associated with several frequently used exfoliation methods, which not only increase the cost but also introduce inadvertent defects in the final product. Surfactant gel assisted exfoliation of graphite can be an attractive substitute for the conventional surfactant based exfoliation methods since it is quick and does not require any additional driving forces. The synthesis protocol is extremely simple and can be performed at low temperatures. Additionally, the gel can also serve as a storage media; exfoliated graphene can be stored in it for prolong durations.

Herein, we report a multifaceted methodology for the preparation of different kind of nanomaterials. Proposed synthesis methodology explores oil swollen gelatinous micelles as a reaction medium and exfoliation medium for the fabrication of the metal NPs and graphene, respectively. Unlike several other previously practiced chemical methods, current method is not limited to inorganic or carbonic materials and can be employed for both types of materials universally.

2. Materials and methods

2.1. Materials

All the chemicals, including Auric chloride ($AuCl_3$) (Alfa aesar chemicals), Silver nitrate ($AgNO_3$) (CDH chemicals), Cetyltrimethylammonium bromide (CTAB) (Spectrochem chemicals), Tween 80 (Fischer scientific chemicals), n-hexane (RANKEM chemicals), Graphite (Alfa aesar chemicals), were used as received without any further purification. All solutions were prepared using de-ionized water.

2.2. Methods

2.2.1. Preparation of Au, Ag and Au-Ag nanoparticles in tween-80 based gels

2 gm tween 80 and 6 ml n-hexane were mixed in a beaker, the temperature of as prepared reaction mixture was maintained at ~35 °C. 2 ml 0.005 M $AuCl_3$ aqueous solution was quickly added to the reaction mixture under continuous stirring, which led to the formation of a thick gel (Fig. 1a). The beaker containing gel was tightly covered to avoid evaporation of its fluid content and left for 5 h. Light yellow color[1] gel turned into violet color after 5 h (Fig. 1b) thereafter gel was dissolved in water, which resulted violet color turbid suspension of Au NPs (Fig. 1e). Half volume of the Au NPs suspension was heated at 80 °C till it turns into clear violet color suspension (Fig. 1f). For the synthesis of Au NPs within hexane less tween 80 gel same composition of reaction mixture was used except n-hexane was not added in the reaction mixture and gel was left for 12 h to complete the Au NPs formation (Fig. 1c) after addition of 2 ml 0.005 M $AuCl_3$ aqueous solution to tween 80. As prepared Au NPs containing gel was dissolved in water to produce red color suspension (Fig. 1g). For the preparation of Ag NPs within tween 80 gel, 1 ml aqueous solution of $AgNO_3$ and Ascorbic acid each were added simultaneously to the reaction mixture containing 2 gm tween 80 and 10 ml n-hexane, with a preset temperature ~35 °C. Different concentrations of $AgNO_3$ and Ascorbic acid (0.01, 0.02, 0.03, 0.04, 0.05 M) were tried for the synthesis of Ag NPs. Addition of salt solution immediately produces a green color thick gel (Fig. 1d), which was dissolved in water in order to obtain nanoparticles suspension (Fig. 1i). In case of Ag NPs, external reducing agent ascorbic acid was used since tween 80 is not capable of reducing Ag^+ to Ag metal. For the synthesis of Ag-Au NPs, 2 gm tween 80 was mixed with 6 ml n-hexane the temperature of the reaction mixture was maintained at 35 °C. 1 ml each of $AuCl_3$ (0.005 M) and $AgNO_3$ (0.005 M) aqueous solutions was added to the tween 80/n-hexane mixture which led to formation of a gel. As prepared gel was left at room temperature for 5 h, afterwards it was dissolved in water to make suspension of Au NPs containing $AgNO_3$. Thereafter $AgNO_3$ containing Au NPs suspension was heated at 80 °C till it turns into clear violet color suspension. 1 ml 0.05 M Ascorbic acid was added to the above prepared $AgNO_3$ containing Au NPs suspension

[1] For interpretation of color in Figs. 1 and 4, the reader is referred to the web version of this article.