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Oil swollen surfactant gel based synthesis of metal oxides nanoparticles: An attractive alternative for the conventional sol gel synthesis

Ravi Kant Upadhyay [a], Santanu Pan [b], Anjan Barman [b], James A. McLaughlin [c], Susanta Sinha Roy [d,*]

[a] Department of Chemistry, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India
[b] Department of Condensed Matter Physics and Material Sciences S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700098, India
[c] Nanotechnology and Integrated Bioengineering Centre (NIBEC), University of Ulster at Jordanstown, Shore Road, Newtownabbey BT37 0QB, United Kingdom
[d] Department of Physics, School of Natural Sciences, Shiv Nadar University, Gautam Budh Nagar 201314, Uttar Pradesh, India

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ABSTRACT

Metals (Zr, Zn and Cu) containing oil swollen surfactant gels have been utilized as precursors for the preparation of metal oxides (ZrO_2, ZnO and CuO) nanoparticles. No metal alkoxide, external gelating agent or any other intricate molecule have been utilized to reinforce gelation; gel stage has been achieved simply through judicial adjustment of water to surfactant ratio and salinity of the reaction mixture. Unlike, several previously published reports, in this approach surfactant has been added not to just increase the viscosity of solution but it has also formed rod shaped gelatinous micelles in response to the variation in water to surfactant ratio, which endowed mechanical strength to the gel. The effect of nature of metal salt on mechanical properties of gel has also been investigated. Zn and Cu containing cetyltrimethylammonium bromide (CTAB) gels have been found to be strongest and weakest, respectively. Metal containing CTAB gels were heat treated at various temperatures (600, 700 and 800 °C) in order to obtain metal oxides nanoparticles. The effect of calcination temperature on crystallinity, particle size and morphology of the metal oxides nanoparticles has also been investigated. A comparison between ZrO_2 nanoparticles prepared using conventional sol gel and oil swollen surfactant gel method has also been carried out in terms of crystallinity, particle size and optical property.

1. Introduction

Sol gel is one of the most common and practiced approach for the synthesis of metal oxide nanoparticles (NPs) [1–3]. In conventional sol gel method, metal alkoxide sol undergoes hydrolysis followed by condensation which results metal containing rigid gelatinous mass. Heat treatment of as obtained gels results formation of metal oxide nanoparticles. Most of the sol gel methods require metal alkoxides as metal precursors which are very much costly, unstable and not environment benign [4]. High cost and unstability of metal alkoxide precursors are two shortcomings associated with the traditional sol gel method which limits its utility as a method for the large scale preparation of metal oxide nanoparticles [3]. These shortcomings associated with the traditional metal alkoxide mediated sol gel synthesis propelled researchers to find alternative approaches in which stable metal salts can be utilized and sol-gel transition can be achieved by reaction of salts with simple complex forming molecules such as citrate [5], oxalic acid [6], ethylenediaminetetraacetic acid (EDTA) [7], glucose [8] and propylene oxide [9] etc. In category of metal alkoxide less sol gel synthesis pechini method, which involves combination of citric acid with ethylene glycol, has been explored most frequently [10,11]. This method involves esterification between citrate and ethylene glycol which endows gel-like nature to the reaction mixture. Several modifications in the reactant composition such as replacement of citric acid with other di, tri and tetra carboxylic acid or ethylene glycol with other polyols and polymers, have been tried to improve the quality of final product [3,12–14]. In most of the abovementioned sol gel methods water content plays a crucial role in gel formation, recently non-aqueous sol gel method involving solvents other than water such as alcohol, ether and ketone have also been utilized for the metal oxide nanoparticles synthesis [15–17].

Surfactant gel assisted synthesis can be an attractive alternative

* Corresponding author.
E-mail address: susanta.roy@snu.edu.in (S.S. Roy).

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for the conventional sol gel method for preparation of metal oxide nanoparticles. Surfactant gels are easy to prepare and require surfactants which are cost effective and easily available. Unlike conventional sol gel method surfactant gels donot require metal alkoxides as metal precursors for the formation of gels and can be obtained easily through precise control of water to surfactant ratio and salinity. Furthermore the concentration of metals in gel can be varied according to need while keeping the amount of gel constant on the other hand conventional sol gel method doesnot give liberty of changing the concentration of metals since percentage of metals per volume of alkoxide precursor is always fixed. Unlike sol gel method surfactant based gels can be reversible, these gels can be dried by simple evaporation of its fluid content and gel stage can be restored by maintaining the same ratio of water/surfactant/oil phase. Previously, Surfactant gels have been proven to be highly efficient for the preparation of porous oxide materials [18,19]. Metal containing surfactant gels have also been explored as media and electrolytes for the growth and electro-deposition of oxides, respectively [20,21].

Herein, we report a fast and facile oil swollen surfactant gel based synthesis for the metal oxides nanoparticles preparation. Metals (Cu, Zn and Zr) containing cetyltrimethylammonium bromide (CTAB) gels have been fabricated by judicial control of water to surfactant ratio without using any metal alkoxides and other complex gelating molecule. Proposed synthesis approach can be a cheap alterative for the conventional sol gel method. Metal oxides (CuO, ZnO and ZrO_2) nanoparticles synthesized using surfactant gel method can be useful for variety of applications, such as CuO and ZnO can be utilized as photocatalyst while ZrO_2 NPs can be used as adsorbent for the removal of waterborne pollutants. Apart from environmental applications CuO and ZnO can also serve as an electrode material for the fabrication electrochemical devices such as batteries and capacitors. ZrO_2 NPs can be explored as refractory material and catalyst support also.

2. Experimental

2.1. Materials

All the chemicals, including Zirconium oxychloride ($ZrOCl_2$ $8H_2O$) (CDH chemicals), Zirconium (IV) butoxide (TCI Chemicals), *n*-butanol (RANKEM chemicals), Ammonia (RANKEM chemicals), Zinc acetate ($Zn(CH_3COO)_2$ $2H_2O$) (RANKEM chemicals), Copper sulfate ($CuSO_4$ $5H_2O$) (RANKEM chemicals), Cetyltrimethylammonium bromide (CTAB) (Spectrochem chemicals), n-hexane (RANKEM chemicals), were used as received without any further purification. All solutions were prepared using de-ionized water.

2.2. Preparation of Zr, Zn and Cu containing CTAB gels and oxides

For the preparation of Zr and Zn containing CTAB gels, two batches of 7.80 g CTAB in 50 mL n-hexane was prepared, the temperature of reaction mixtures was maintained ~35 °C. 10 mL aqueous solution of $ZrOCl_2$ (1.04 M) and Zn $(CH_3COO)_2$ (1.52 M), was added separately to the above prepared reaction mixtures. Addition of aqueous solution of Zr and Zn salts resulted quick formation of the gels (Fig. 1a, b). Gel formation causes rise in the viscosity of reaction mixture and magnetic bit gets trapped in the gel therefore after gel formation, a spatula or glass rod was used to stir the gel. For the preparation of Cu containing CTAB gel, same procedure was followed, except the amount of CTAB was increased up to 8.80 g. Addition of 12 ml $CuSO_4$ aqueous solution (1.31 M) to the CTAB and n-hexane mixture, produced a dark blue color gel (Fig. 1(c)). In case of Cu, gel formation is slow since higher water content has been utilized so after addition of the aqueous salt solution, reaction mixture was mixed using spatula and left for 15 min to complete the gelation. As prepared Zr, Zn and Cu containing CTAB gels were dried by heating at 70 °C on a hot plate, producing light yellow, white and light blue colored powder for Zr, Zn and Cu containing CTAB gels, respectively. As obtained Zr, Zn and Cu containing powders were further grinded and heated at different temperatures (600, 700, 800 °C) for 2 h in a muffle furnace to obtain metal oxides (ZrO_2, ZnO and CuO) nanoparticles.

2.3. Preparation of ZrO_2 nanoparticles using sol gel method

5 mL n-butanol was mixed with 2 mL Zirconium (IV) butoxide, as prepared reaction mixture was stirred for 10 min. 500 μL of aqueous ammonia was added to the above prepared reaction mixture under continuous stirring which was followed by addition of 150 μL of water resulting formation of a milky white gel. As obtained gel was dried in an air oven at 80 °C thereafter dried gel was grinded to form powder which was further annealed at 800 °C for the formation of ZrO_2 NPs.

2.4. Characterization

FTIR measurements of gels, its content, metal precursors and metal oxides samples, were carried out using ATR FTIR spectroscopy (Thermo Scientific Nicolet™ iS™5 FTIR) with diamond ATR accessory. Gel samples were taken out from the sealed containers and immediately mounted on the ATR crystal. The temperature of

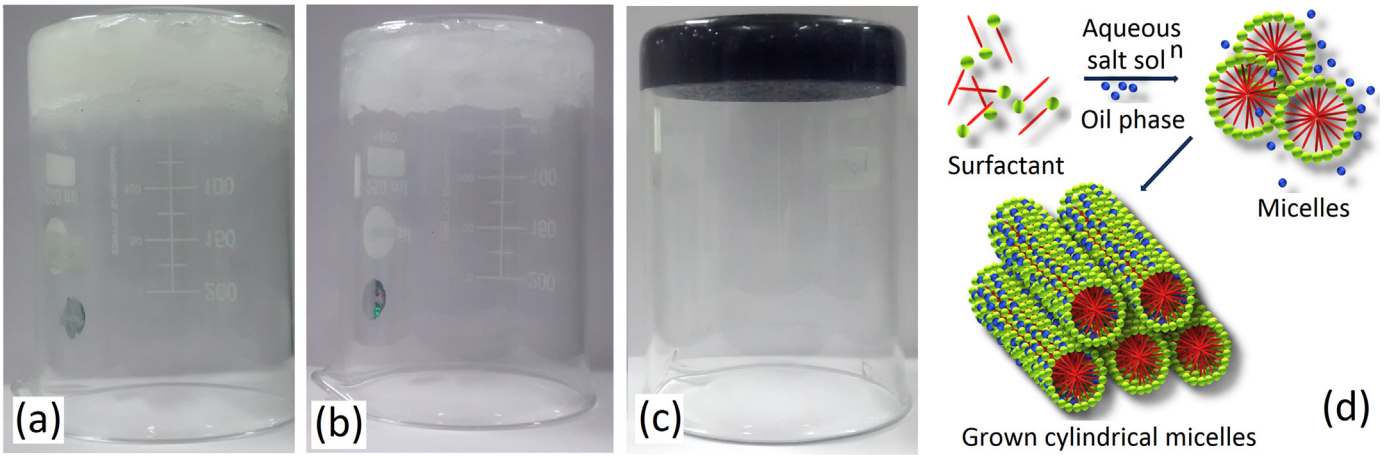

Fig. 1. Real pictures of (a) Zr containing CTAB gel (b) Zn containing CTAB gel (c) Cu containing CTAB gel and (d) mechanism of gel formation.