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# Nanocrystalline Janus films of inorganic materials prepared at the liquid–liquid interface

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ABSTRACT

The interface between toluene and water has been employed to prepare ultrathin Janus nanocrystalline films of metal oxides, metal chalcogenides and gold, wherein the surface on the organic-side is hydrophobic and the aqueous-side is hydrophilic. We have changed the nature of the metal precursor or capping agent in the organic layer to increase the hydrophobicity. The strategy employed for this purpose is to increase the length of the alkane chain in the precursor or use a perfluroalkane derivative as precursor or as a capping agent. The hydrophobicity and hydrophilicity of the Janus films have been determined by contact angle measurements. The morphology of hydrophobic and hydrophilic sides of the film have been examined by field emission scanning electron microscopy.



## 1. Introduction

Several surfaces in nature, including plant leaves [1,2], legs of the water strider [3], troughs on the elytra of desert beetles [4], and gecko's feet [5,6] are superhydrophobic, displaying contact angles with water greater than 150°. Synthesis of such superhydrophobic surfaces in the laboratory is of technological and academic interest [7–9]. It is also challenging to transfer such films to another substrate such as glass, silicon and cloths. Films with one side surface is highly hydrophobic and another side is hydrophilic are termed as Janus films by analogy with Janus particles or cylinders [10–14]. Janus films may have many potential applications such as where a surface or coating with markedly asymmetric wetting properties is desirable, unlike hydrophilic silicon wafer or hydrophobic Teflon, where only one type of wetting property is available. In the case of hydrophilic silicon wafer and hydrophobic Teflon, it can be possible to get only one type of wetting properties. The organic–aqueous interface has been exploited recently for obtaining ultrathin nanocrystalline films of a variety of inorganic materials [15,16]. The method involves dissolving an organic precursor of the relevant metal in the organic layer and the appropriate reagent in the aqueous layer. The product formed by the reaction at the interface contains ultrathin nanocrystalline films of the relevant material. It has been suggested that Janus films can be prepared at the organic–water interface [16] and Kulkarni et al. [17] have recently reported Janus silica films at the oil–water interface by using methyltrimethoxysilane as the silica precursor. We considered that the organic–aqueous interface can actually provide a general method of preparing nanocrystalline Janus films of several inorganic materials. We have therefore generated thin films of metal oxides such as $SiO_2$, $TiO_2$ and $ZrO_2$, metal sulfides such as CdS, ZnS and CuS as well as of gold by employing appropriate precursors and determined the hydrophobicity or hydrophilicity by contact angle measurements. In order to increase the hydrophobicity of the surface on the organic side, we have used precursors possessing long alkane chains or perfluoroalkane chains. The results have been encouraging in that we have obtained Janus films of several materials with significant hydrophobicity of the surfaces on the organic side of the interface.

## 2. Materials and methods

The basic synthetic strategy to prepare Janus oxide films is the hydrolysis of relevant metal precursors dissolved in organic medium by aqueous acid or water at the interface. In order to prepare $SiO_2$ films, 10 mL of toluene and 10 mL of water were taken in a 25 mL beaker. After waiting for a few minutes to stabilize the interface, 200 μL of tetraethylorthosilicate (TEOS) and 100 μL of concentrated hydrochloric acid were added to the toluene and water layers respectively and kept the beaker in ambient conditions. After 24 h a white colored thin film was formed at the interface. We have also used hexadecyltrimethoxysilane or perfluo-

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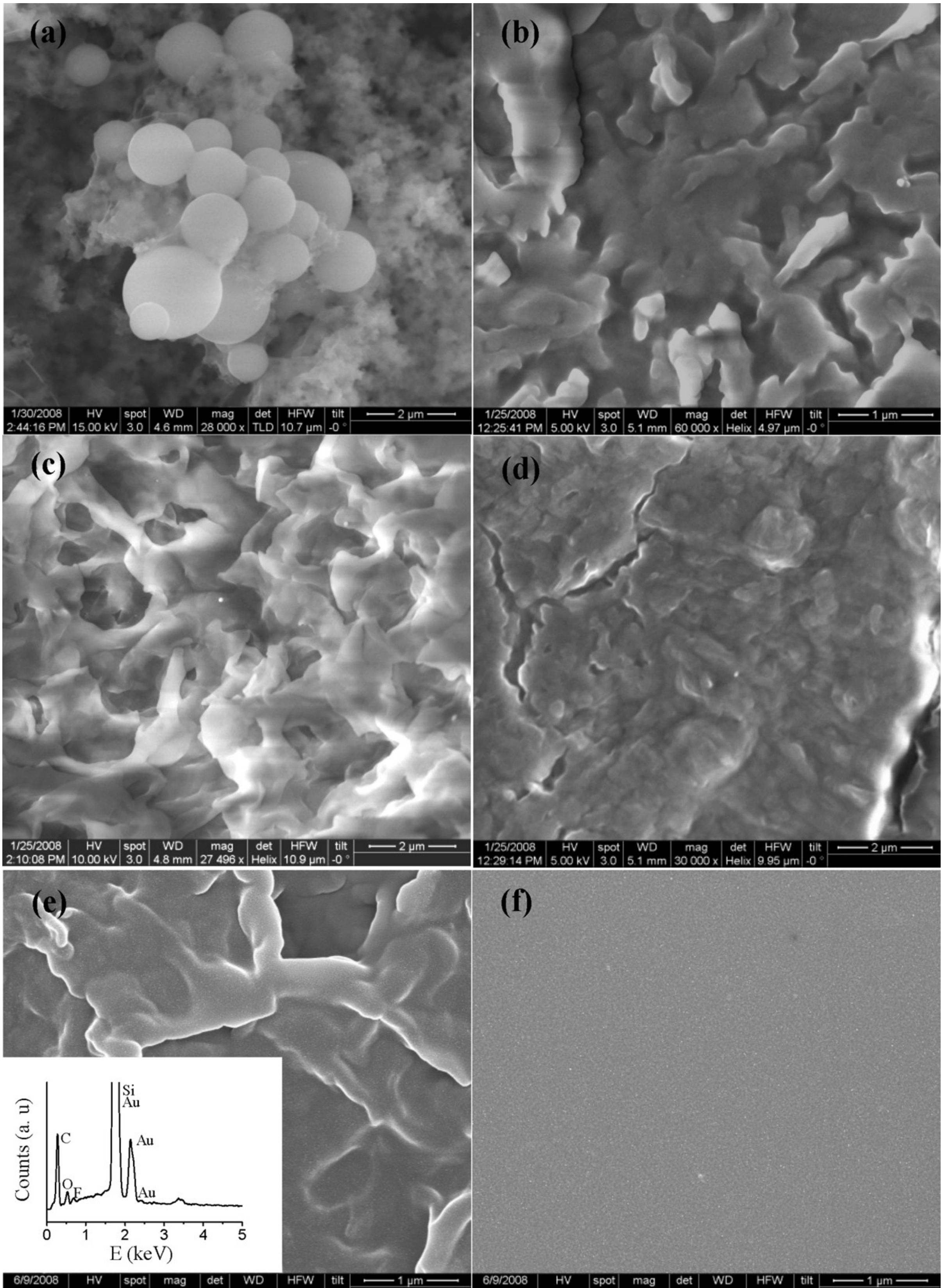


**Fig. 1.** (a) and (b) FESEM images of toluene- and water-side surfaces of the $SiO_2$ film prepared from tetraethylorthosilicate. (c) and (d) FESEM images of toluene- and water-side surfaces of $SiO_2$ film prepared from hexadecyltrimethoxysilane. (e) and (f) FESEM images of toluene- and water-side surfaces of the $SiO_2$ film prepared from perfluorooctyltrimethoxysilane. Inset in (e) shows the EDAX spectrum of the corresponding film.

rooctyltrimethoxysilane as the Si precursor, keeping the other conditions the same. In order to prepare $TiO_2$ films, 10 mL of toluene and 10 mL of water were taken in a 25 mL beaker. 50 μL of titanium iso-propoxide was added to the toluene layer and kept