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SHORT COMMUNICATION

**Synthesis of copper nanoshales from a Triton™
X-100/cyclohexane/water ternary microemulsion system**

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Abstract: A shale-like copper nanostructure was synthesized for the first time from a water-in-oil microemulsion medium comprising Triton™ X-100/cyclohexane/water ternary system. The nanoshales were synthesized through chemical reduction by hydrazinium hydroxide in alkaline medium. The nanoshales were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

Keywords: metal nanostructure; reverse micelle system; copper nanostructure; water in-oil microemulsion.

INTRODUCTION

The synthesis of transition metal nanostructures with different sizes and shapes has been of interest in recent years due to their unique properties, such as surface, quantum size, catalytic and volume effects.^{1–4} The shape, size and morphology of nanostructured materials, which determine their properties and activities, depend on the synthesis method. Among the transition metals, copper nanostructures are of considerable interest because copper has many important applications in medicine^{5,6} and modern technologies.⁷ Copper nanostructures have been synthesized by various methods such as ion reduction,⁸ thermal decomposition,⁹ microwave-assisted,¹⁰ supercritical,¹¹ laser ablation,¹² surfactant-assisted electrodeposition¹³ and sonochemical reduction.¹⁴

Reverse microemulsion systems comprise an aqueous phase as droplets dispersed in an oil phase by means of a surfactant(s), in which the polar heads of the surfactant are accumulated in the interior part, and the lipophilic tails extend outwards into the oil phase. Therefore, tiny droplets of aqueous phase are encap-

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sulated as reverse micelles. From a molecular viewpoint, reverse micelles are heterogeneous; however, they are thermodynamically stable. Microemulsions are suitable reaction media for the synthesis of nanostructures due to limitations in the volume of the micelles that act as microreactors. The size of the micelle can be controlled by the mole fraction of the microemulsion components.¹⁵ Microemulsions are widely used in the synthesis of metal and alloy nanostructures.^{16,17}

In this research, copper nanoshales were synthesized through chemical reduction in a water-in-oil microemulsion medium.

EXPERIMENTAL

All employed chemicals were of analytical grade from Merck or Sigma and used without further purification. For the synthesis of copper nanoshales, two similar microemulsions, I and II, were prepared. Microemulsion I was composed of 2 mmol Triton™ X-100, 25 mL cyclohexane and 5 mL of an aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (containing 1.0 mmol copper). Microemulsion II was composed of 2 mmol Triton™ X-100, 25 mL cyclohexane and 5 mL of an aqueous solution of NaOH (containing 3.0 mmol alkali) + hydrazinium hydroxide (containing 20 mmol hydrazine). The two microemulsions were purged with nitrogen gas. Then, microemulsions I and II were mixed and stirred for 2 h under a constant stream of nitrogen gas to produce an inert atmosphere. The solid black-brown product that formed was washed with redistilled water and ethanol and dried under vacuum.

Scanning electron microscopy (SEM) was performed using an X-30 Philips instrument. Powder X-ray diffraction (XRD) patterns were recorded at a scanning rate of $2.4^\circ \text{ min}^{-1}$ on a Philips X'Pert X-ray diffractometer (The Netherlands) with a CuK_α radiation at 40 kV and 30 mA. Thermal properties of the microemulsion were investigated using differential scanning calorimetry (DSC, Mettler Toledo DSC 1, Switzerland) over a scanning range of -30 to 30°C at $10^\circ \text{C min}^{-1}$. The size of water droplets in the microemulsion was measured using a Scatterscope particle size analyzer (Korea).

RESULTS AND DISCUSSION

The results of the thermal analysis of the microemulsion by DSC are shown in Fig. 1A. A broad endothermic peak in the range -2 to 10°C was observed. This melting endotherm is related to melting of the components of the microemulsion. As the melting points of these components are similar (Triton™ X-100: $\approx 5^\circ \text{C}$, cyclohexane: 6.5°C , water: 0.0°C), the melting events appeared as a single broad peak. The probabilities of the sizes of the droplets in the microemulsion are presented in Fig. 1B. Based on the results, the mean size of the droplets was 605 nm.

The SEM images of the as-synthesized copper nanoshales are shown in Fig. 2. Thin sheets of ≈ 100 nm thickness were observed. The samples were comprised of quadrangular- or lozenge-like flakes that were relatively adhered together and resembled nanoshales.

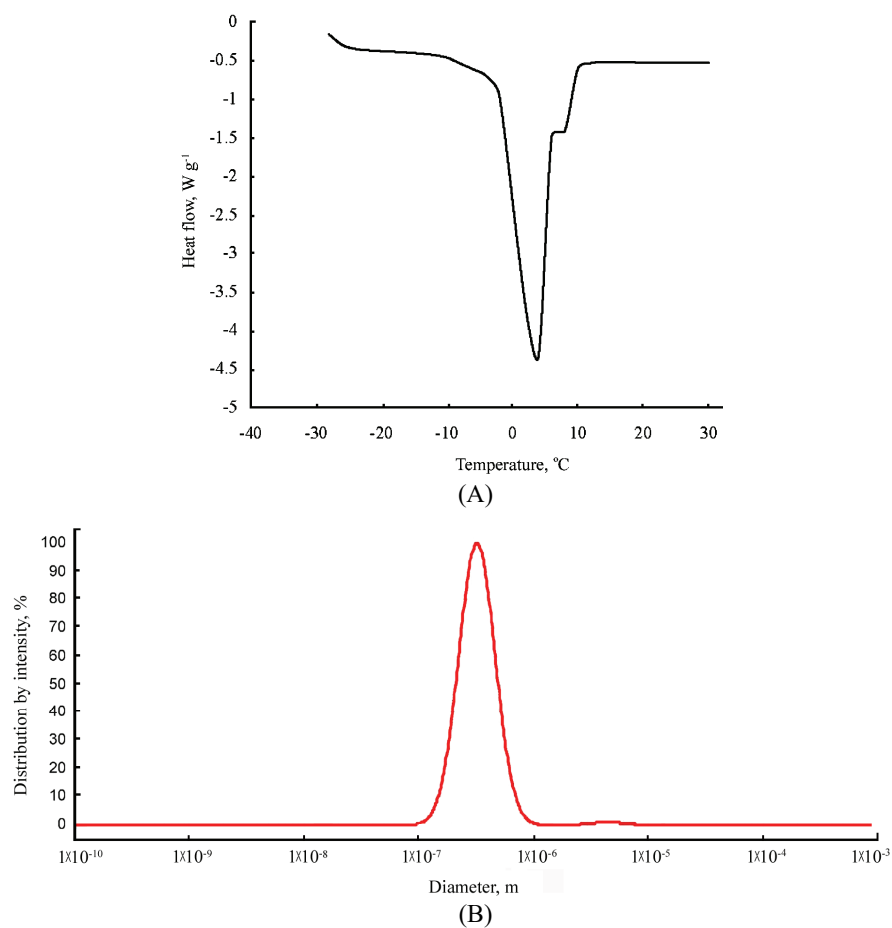


Fig. 1. A) DSC curve for the microemulsion and B) the probabilities of the sizes of the droplets in the microemulsion.

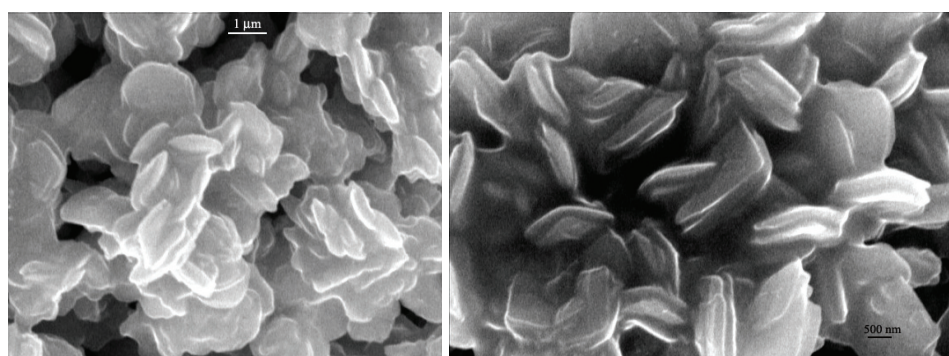


Fig. 2. SEM images recorded for the copper nanoshales.

The IR spectrum recorded for the copper nanoshales (Fig. 3) showed no characteristic peaks related to organic functional groups. This indicates that the nanoshales were free from components of the microemulsion and no surface adsorption of organics occurred on the surface of the nanoshales.

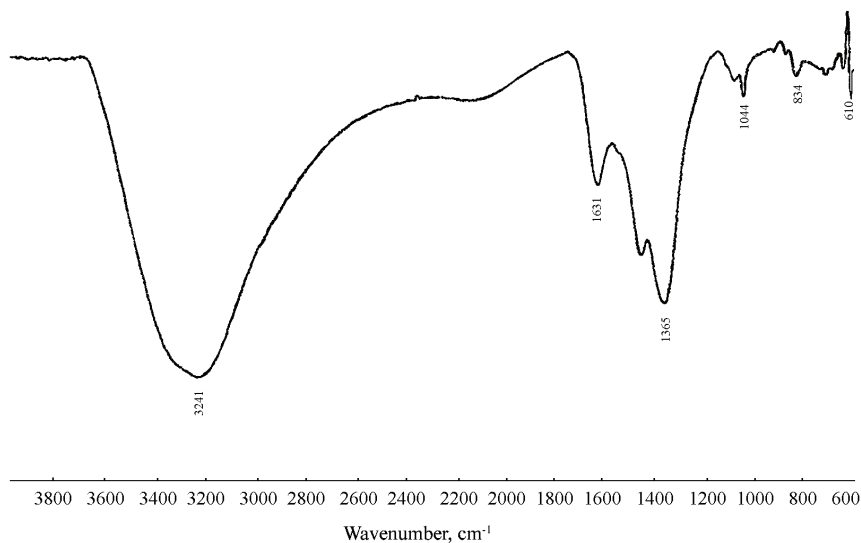


Fig. 3. IR spectrum recorded for the copper nanoshales.

An XRD pattern of the copper nanoshales is shown in Fig. 4. All the peaks could readily be assigned to pure copper (JCPDS file No. 04-0836). In the pattern, the main diffraction peaks at 42.6, 50.8 and 74.3° were indexed to (111), (200) and (220) reflections, respectively. In addition, the average grain size of the

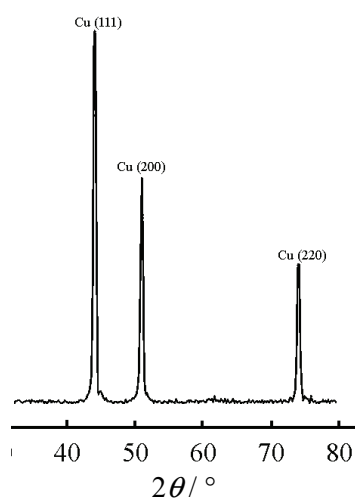


Fig. 4. XRD spectrum recorded for the copper nanoshales.

nanoshales was obtained as ≈ 32 nm based on the half width of the strongest diffraction peak and using the Debye–Scherrer formula. The pattern also showed no evidence of oxides, indicating the purity of the sample.

In order to inspect the reaction mechanism, hydrazinium hydroxide was not added to microemulsion II. In this case, after the mixing of the two microemulsions, the color of the mixture first turned dark green and then black after several minutes. The XRD pattern of the black product is presented in Fig. 5. In the pattern, the main diffraction peaks at 31.7 , 35.5 , 38.5 , 48.7 , 53.5 , 58 , 61.5 , 66 , 68 , 75 and 82.6° are indexed to (110), (111), (111), (202), (020), (202), (113), (310), (113) and (004) reflections, respectively. The peak positions were in good agreement with the standard diffraction data (JCPDS file No. 05-0661) of copper oxide with a monoclinic phase. In the pattern, no peak ascribed to Cu_2O was detected, indicating that copper(II) oxide was formed.

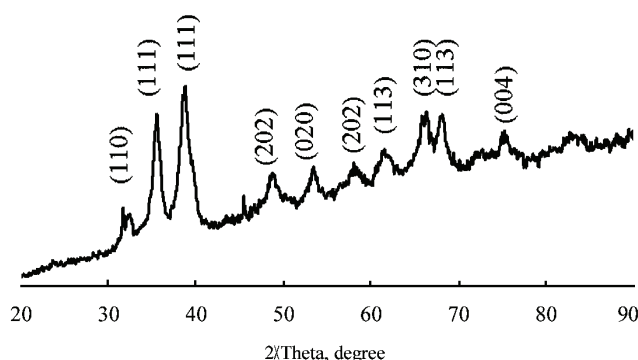
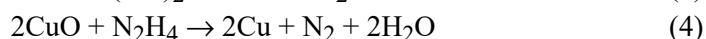
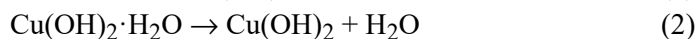
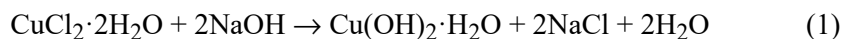


Fig. 5. XRD spectrum recorded for copper oxide.

It could be suggested that the whole reaction occurred as follows. After addition of the two microemulsions, copper(II) hydroxide precipitated first and then quickly dehydrated into copper(II) oxide. The XRD results revealed that the black precipitates were copper(II) oxide. In the next step and at a slower rate, the black precipitate was reduced to copper nanoshales. It should be noted that the special shape of the copper nanostructure directly resulted from the shape-directing and shape-controlling abilities of the microemulsions.

The chemical reactions involved in the synthesis procedure are:



CONCLUSION

Copper nanoshales were synthesized from a ternary microemulsion system of Triton™ X-100/cyclohexane/water. This microemulsion medium led to the formation of copper with a unique shape because the microreactors had shape and size directing abilities. The employed method could be extendable to the synthesis of other shapes and sizes of copper species from other microemulsion systems, or to other metal nanostructures using the microemulsion employed in this study.

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ИЗВОД

СИНТЕЗА БАКАРНИХ НАНОШКРИЉАЦА ИЗ ТРОЈНОГ МИКРОЕМУЛЗИОНОГ СИСТЕМА TRITON™ X-100/ЦИКЛОХЕКСАН/ВОДА

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По први пут синтетисан је бакар наноструктуре налик шкриљцима у микроемулзионој средини вода/уље коју чини тројна смеша Triton™ X-100/циклохексан/вода. Нанешкриљци су синтетисани редукцијом Cu(I)-оксида хидразином у алкалној средини. Нанешкриљци су карактерисани скенирајућом електронском микроскопијом и дифракцијом X-зрака.

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