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Hierarchically ordered CdS doped nanoporous membrane†

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Large-dimension heterogeneous nanoporous membranes were obtained by the formation of CdS doped mesoporous silica within the porous channels of alumina membranes.

Porous materials with nano-sized pore diameter have attracted great attention in many areas of heterogeneous catalysis,[1] molecular separation,[2] and composite nanomaterials[3] due to their unique properties. To date, mesoporous materials which have pore sizes of a few nanometers have been developed with various compositions of metal oxides[4] and semiconductors.[5] Such mesoporous materials were typically prepared as a powder type consisting of particles in micrometers. Therefore, the aligned pattern of the mesoporous channels could not be achieved in large scale dimensions. Since the membrane (or film) type mesoporous materials of a few nanometer pore size have the feature of unidirectionally ordered mesoporous channels which have many advantages in the science and technology aspects of functional properties oriented in large dimensions, many studies have been tried to obtain free-standing mesoporous films of a few nanometer pore size.[6]

Very recently, a free-standing nanoporous membrane of hierarchically ordered porous structure which has the pore size of 3 nm was made by utilizing a self-organized template of surfactant molecules in the pore channels of porous alumina, and the obtained nanoporous membrane presents a size-selective molecular sieving effect in a few nanometer range.[7] Such nanoporous membranes with through-pore channels have high potential for other applications (molecular catalytic reactions, sensors, *etc.*) if a proper functional group is introduced into the membrane.

In this study, we present CdS doped hierarchical nanoporous membrane filters (pore size = ~6 nm, domain area = ~5 cm^2) which show the optical characteristics of CdS semiconductors in the visible spectral range.

Porous alumina membranes (Whatman, Anodisc) that have an averaged pore diameter of 200 ± 20 nm, a membrane dimension of ~5 cm^2, and a thickness of 60 μm were utilized as the templates for the fabrication of the hierarchical nanoporous structures. The lyotropic precursor solution consisted of the Pluronic F127 ($EO_{106}PO_{70}$ EO_{106}) triblock copolymer (BASF) and the silica and cadmium precursors were incorporated into the nanochannels of the porous alumina. After incorporation of the lyotropic precursor solution into the nanoporous alumina membrane and subsequent gelation, the resulting alumina membrane was exposed to H_2S. The final membrane product presents the characteristic yellow colour of the CdS component which is doped into the mesoporous silica framework confined within the nanochannels of the rigid porous alumina template. 1 and 3 mol% of CdS to the SiO_2 source were applied in the lyotropic systems to produce mesoporous silica doped with different contents of the CdS.

Fig. 1 shows the field-emission scanning electron microscopy (FE-SEM) images of the CdS doped (1 mol%) silica nanostructure confined within the porous alumina membrane. The confined CdS doped silica nanostructure represents the fiber morphology. The composite nanofibers are shown to be almost filled within the nanochannels of the porous alumina. After complete removal of the porous alumina template with 1 M solution of aqueous NaOH, the single composite nanofiber clearly indicates the networked mesophase structure with the pore diameter of ~6 nm as shown in Fig. 1C. Moreover, it is noteworthy that an onion-like shell structure is observed in the cross-sectional view of the composite nanofiber (marked by arrow). The hierarchical nanoporous membrane with increased loading level of the CdS (3 mol%) also shows well incorporated nanofiber morphology within the porous alumina, and a unique mesoporous structure is still maintained (see ESI†, Fig. S1).

The CdS doped mesoporous silica in the porous alumina shows several X-ray scatterings in the small-angle region (Fig. 2A). The

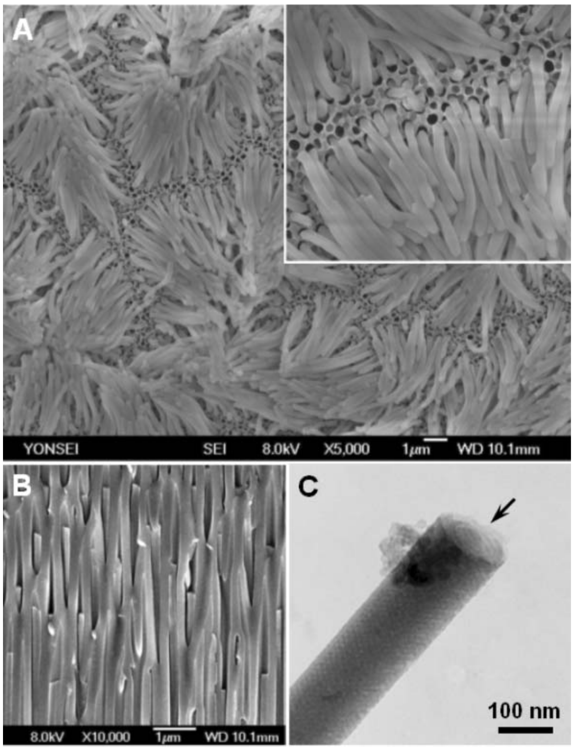

Fig. 1 FE-SEM image of the 1 mol% CdS doped mesoporous nanostructure confined within the porous alumina: (A) top and (B) side views. (C) TEM image of a single mesoporous silica nanofiber including the CdS, which is obtained after removal of the porous alumina template by 1 M of aqueous NaOH.

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† Electronic supplementary information (ESI) available: experimental details, instrumentation, FE-SEM and TEM images for the 3 mol% CdS doped nanoporous membrane, and original small-angle X-ray scatterings. See http://www.rsc.org/suppdata/cc/b4/b410631h/

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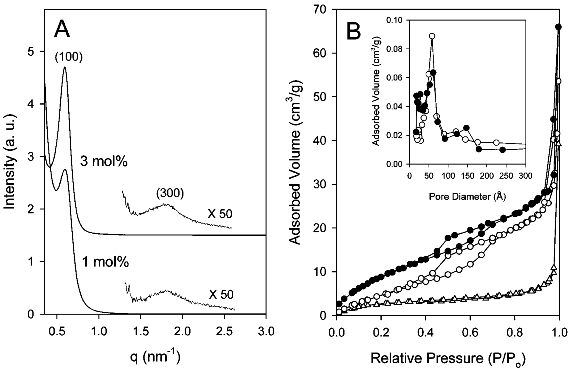

Fig. 2 (A) Small-angle X-ray scatterings for the CdS doped mesoporous silica (the background scatterings of the porous alumina are subtracted) and (B) nitrogen adsorption–desorption isotherms for the CdS doped nanoporous membranes with different doping levels: 1 mol% (open circles) and 3 mol% (filled circles). The nitrogen adsorption–desorption isotherm for the bare porous alumina is also presented (triangles). Inset are the pore diameters estimated by the BJH method.

scattering peaks are well correlated to the lamellar structure (d_{100} = 10.64 nm) for both the composite membranes. Since the X-ray beam is vertically irradiated on the membrane plane (transparent detection mode), such diffractional scattering appears to originate from the unique pseudo-lamellar structure of the onion-like concentric shell of the mesophase nanofiber confined within the porous alumina membrane.

Fig. 2B shows the nitrogen adsorption–desorption isotherms for the CdS doped mesoporous silica within the porous alumina, which shows the characteristic capillary condensation for mesoporous material. From the results, the Brunauer–Emmett–Teller (BET) surface area and pore volume are estimated to be 25.1 m^2 g^{-1} and 0.046 cm^3 g^{-1} for the 1 mol% CdS doped composite membrane, respectively, and these values are slightly increased to 38.6 m^2 g^{-1} and 0.050 cm^3 g^{-1} for the higher CdS doping level of 3 mol%. The major pore diameters estimated by the Barrett–Joyner–Halenda (BJH) method are ~6 nm for both the composite nanoporous membranes (inset of Fig. 2B), which is consistent with the pore diameters estimated from the TEM images. This consistency implies that the core part of the mesoporous structure confined within the porous alumina can be accessible for the gas from outside.

The CdS doped composite nanoporous membranes present the typical absorption transition of CdS in the visible spectral range, whereas the bare porous alumina does not show any significant optical response in the similar spectral region (Fig. 3). It is noted that the 1 mol% CdS doped nanoporous membrane shows the absorption onset at ~460 nm, and the onset for the higher doping level (3 mol% CdS) of the mesoporous membrane is red-shifted to ~480 nm. All the absorption onsets are located at the blue-shifted spectral region from the band-gap absorption (~520 nm) of the bulk CdS,[8] which possibly implies that the doped CdS within the silica framework exhibits a weak quantum size effect. These functionalized nanoporous membranes with the CdS constituent also show broad emissions centered at ~670 nm. Such largely Stokes shifted broad emission is known to be due to the exciton recombination process in the surface emission states of the CdS.[9]

In summary, we have prepared a hierarchically ordered functional nanoporous membrane which consists of CdS doped mesoporous (pore diameter of ~6 nm) silica incorporated within the nanochannels (~200 nm) of a porous alumina support. Such novel hierarchically ordered heterogeneous nanoporous membranes with the optical functionality of the CdS semiconductor provide a promising vision for the development of multifunctional nanocomposite materials which can be utilized for heterogeneous photocatalytic reactions and nanosensor devices with the function of size-selective molecular sieving.

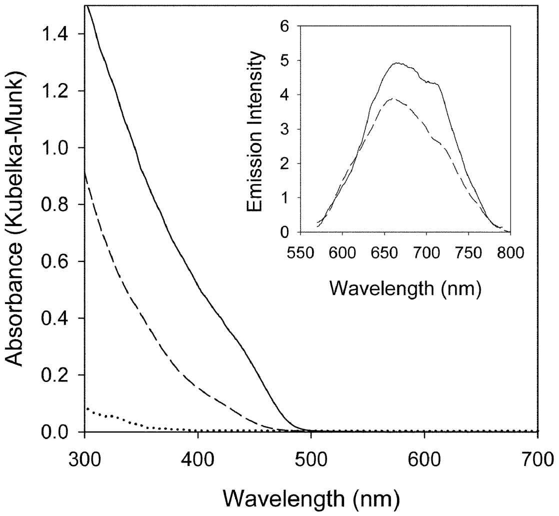

Fig. 3 Absorption spectra for CdS doped nanoporous membranes with different doping levels: 1 mol% (dashed line) and 3 mol% (solid line). The absorption spectrum for the bare porous alumina is also presented (dotted line). The absorption spectra are obtained by applying the Kubelka–Munk function to the diffuse reflectance spectra. Inset are the emission spectra for the CdS doped nanoporous membranes with different doping levels: 1 mol% (dashed line) and 3 mol% (solid line). Excitation wavelength for the emission spectra is 430 nm.

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