Supporting Information

Metal nitride@SiO_2 nanocomposites by sol-gel processing starting from tethered metal complexes

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Experimental

Copper(II) acetate monohydrate ($Cu(OAc)_2 \cdot H_2O$), ethanol and aqueous ammonia (25 wt%) was purchased from Merck, $Si(OEt)_4$ (TEOS) from Fluka, and N-[3-trimethoxysilyl)propyl]ethylenediamine (AEAPTS) and gallium(III) nitrate hydrate from Aldrich, Anhydrous ammonia gas (99.98 %) used for the nitridation was purchased from Messer Austria GmbH. All chemicals were used as received.

Preparation of Cu_3N@SiO_2. To a solution of $Cu(OAc)_2 \cdot H_2O$ in ethanol (10 mL of ethanol per 0.1 mmol of Cu), two equivalent of AEAPTS was added. This resulted in immediate colour change from green to violet blue. The mixture was stirred at room temperature for about 15 min. Twelve equivalents of TEOS was then added to this solution, followed by addition of an amount of 0.2 N aqueous ammonia that corresponded to a 7.5-fold excess of water relative to all alkoxy groups from TEOS and AEAPTS. The resulting homogeneous mixture was heated to 70 ^oC for 72 h in a closed vessel. Removal of the solvent from the obtained gels under reduced pressure gave a blue-coloured gel.

The dry gel was calcined in air at 800 ^oC for 1 h, with a heating rate of 5 ^oC/min. This resulted in a black solid (CuO@SiO_2). Nitridation of CuO@SiO_2 at 300 ^oC for 8 h in a horizontal quartz tube furnace under ammonia atmosphere gave brown Cu_3N@SiO_2. The ammonia flow was maintained at 5 l/h. The sample was taken from the furnace after cooling to room temperature under ammonia atmosphere.

Preparation of GaN@SiO_2. A molar ratio of $Ga(NO_3)_3 \cdot H_2O$ / AEAPTS / TEOS of 1:3:10 was employed. The general procedure for the preparation of the calcined gel was the same as for Cu_3N@SiO_2. Nitridation was achieved through ammonia at 900 ^oC for 3 h with a flow rate of 5 l/h. A yellowish material was obtained after nitridation.

Materials characterization

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209C Iris at heating rate of 10 °C/min under synthetic air.

X-Ray powder diffraction (XRD) measurements were performed on a PANalytical X'Pert PRO Bragg-Brentano X-ray powder diffractometer using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å).

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and energy dispersive absorption X-ray (EDAX) images were obtained using a TECNAI F20-S-TWIN apparatus with field emission source operating at 200 kV. The powders were deposited on a carbon grid for TEM analysis.

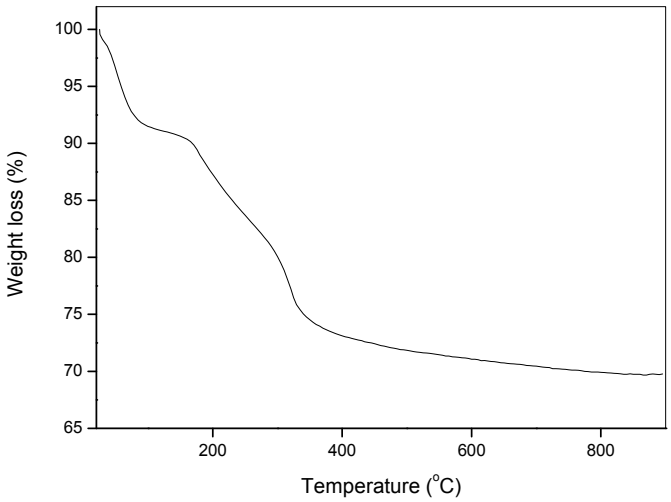

Fig. S1 TGA profile of the dry gel **II**.

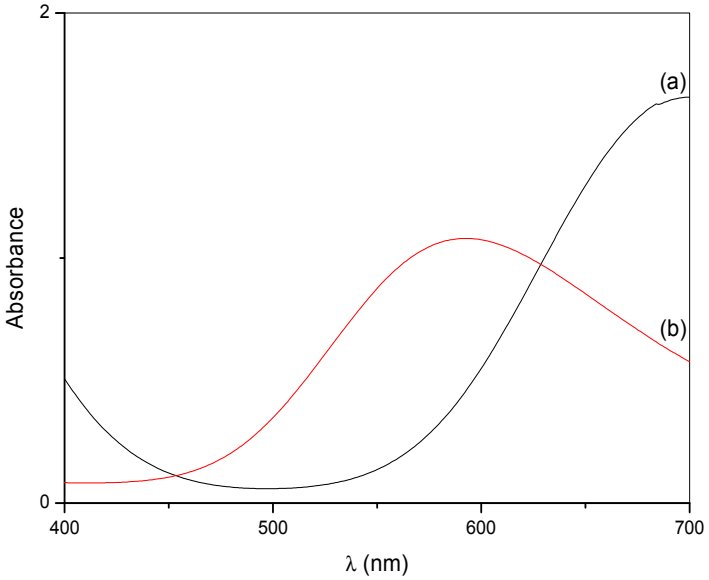

Fig. S2 UV spectra of (a) $Cu(OAc)_2 \cdot H_2O$ in ethanol solution and (b) $Cu(OAc)_2 \cdot H_2O$ and two equivalents of AEAPTS in ethanol solution.

Fig. S3 Photographic image of the obtained gel **II**.