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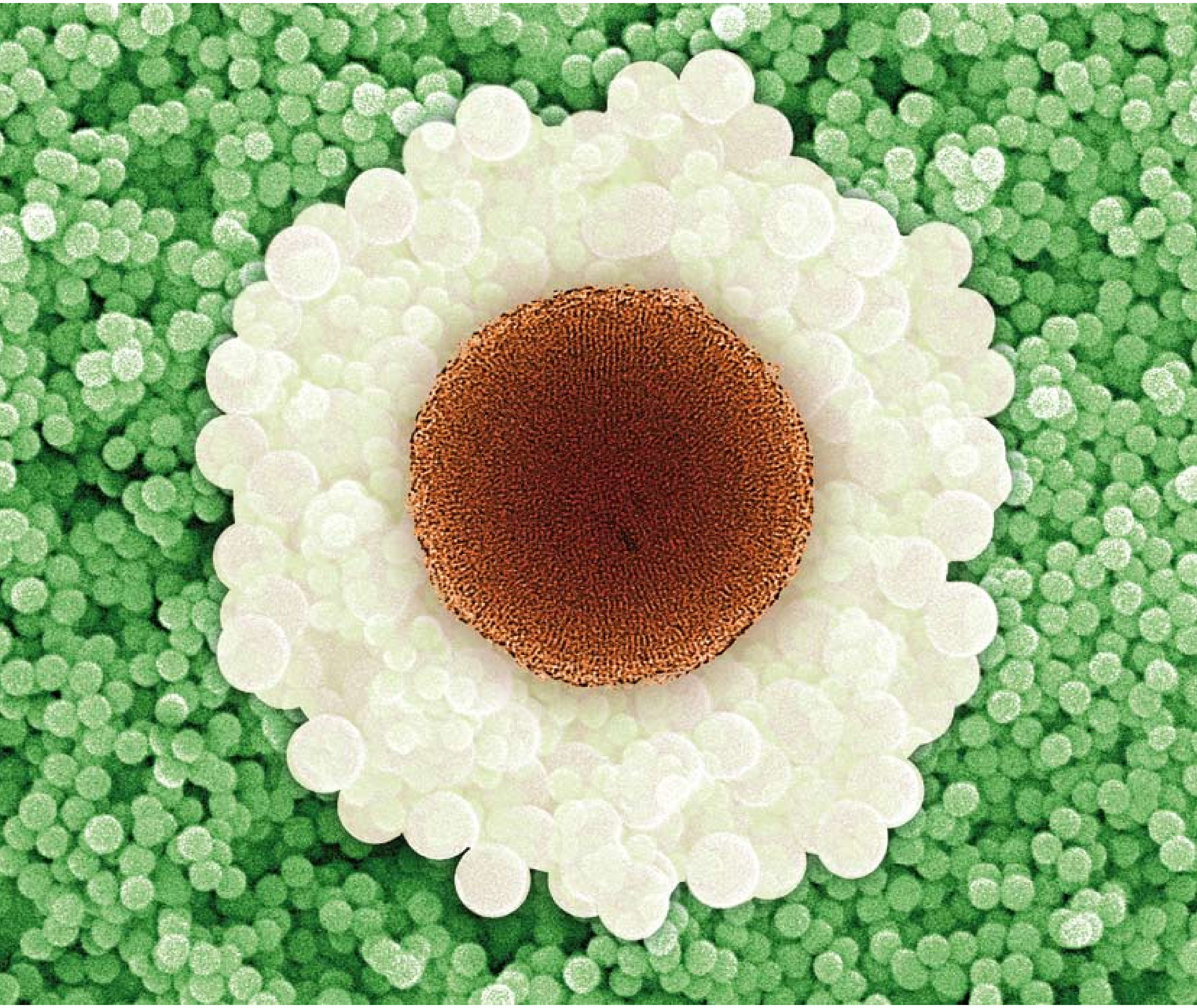

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FEATURE ARTICLE
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Transition metal-catalyzed three-component coupling of allenes and the related allylation reactions

Copper-containing monodisperse mesoporous silica nanospheres by a smart one-step approach†

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Copper-containing mesoporous silica spheres of size in the colloidal range with perfect conservation of pore-ordering, shape and monodispersity and high intra-pore metal dispersion were prepared *via* a new one-step synthesis and functionalisation route.

The morphological and textural control of mesoporous silica materials for the preparation of spherical particles in the submicron size range is of high current interest due to their wide field of applications in many chemical and biological areas. Although mesoporous silica spheres (MSS) have been synthesised using both acid[1] and base mediated pathways, the one-step preparation of particles in the colloidal range has been achieved only in basic conditions. Among the synthesis strategies leading to small mesoporous silica particles,[2] the synthesis of nanosized MSS with a hexagonal MCM-41 type pore ordering typically uses a modified Stöber (basic medium) route, and has been studied for applications in catalysis or controlled drug release.[3] Recently, sub-micrometric MSS displaying a regular radial porosity have been successfully prepared with a high monodispersion factor, allowing their self-assembly into colloidal crystals.[4]

While a large number of publications describe the preparation of metal-functionalised mesoporous silica materials, few reports exist on metal incorporation in sphere-shaped porous particles. Indeed, the base mediated conditions for controllable particle size and morphology are not compatible with common *in situ* incorporation of ionic metal precursors. Direct inclusion of copper has been carried out in the initial synthesis stage through the formation of amino–Cu complexes, which avoids the precipitation of salts in alkaline media and subsequent loss of metal.[5] However this synthesis pathway does not allow adequate control of the material morphology, thus monodisperse spheres have not been obtained. In order to preserve the defined shape of the MSS, transition metal (*e.g.* Pt, Fe derivatives) inclusion in mesoporous silica particles can be achieved by post-synthetic impregnation; nevertheless the backfilling approach risks clogging of the matrix pores, reducing the surface area available.[6]

Here we present the first—to the best of our knowledge—method for *in situ* metal incorporation in mesoporous silica spheres, fully compatible with basic conditions which enable the isolation of perfect monodispersed functionalised nanospheres. In a one-step approach, a copper complex precursor is solubilised in the surfactant template micelles prior to polymerisation to silica. Subsequent template removal leads to copper-containing MSS with a high specific surface area. In this method the copper is brought directly into the pores and is expected to be highly available at the internal surface. Moreover the radial porous texture of these MSS provides a high accessibility to the functionalities, as the entire outer surface of the particles is porous, whereas most of the outer surface of MCM-41 type particles is covered by silica walls.[7]

The monodisperse copper-functionalised MSS were prepared using a facile *one-step* method. In a typical synthesis procedure, 1.36 mmol dodecyltrimethylammonium bromide (Aldrich, 99%) was dissolved in 100 g solution of water and ethylene glycol used as co-solvent (Fluka, >99.5%). The mass ratio of water/ethylene glycol was 1 : 3. Then copper(II) acetylacetonate (Aldrich, >99.99%) dissolved in chloroform (SDS, >99.9%) was added and the mixture was stirred at 313 K. After complete micellar solubilisation of the copper precursor, the addition of 3 mmol of tetramethoxysilane (Aldrich, >99%) was performed under vigorous stirring. The mixture was stirred overnight and the resulting light green precipitate was recovered by centrifugation and dried at 323 K. Template removal from copper-containing MSS was carried out by calcination in air. The sample was heated at a rate of 2 °C min^{-1} to 623 K and maintained at this temperature for 5 h, then cooled to room temperature. The template removal is complete and has been controlled using thermogravimetric analysis (see ESI†). To allow the formation of spherical-shaped nanoparticles, the hydrolysis and condensation of the silicon alkoxide must be carried out in basic conditions, and the pH was adjusted to 12 with sodium hydroxide (Fluka, 99%). The size and morphology of the particles were determined by transmission electron microscopy (TEM), while surface and pore structure parameters were derived from nitrogen adsorption measurements and the content and surface availability of metal species characterised by atomic absorption spectroscopy (AAS) and temperature-programmed reduction (TPR).[8]

TEM micrographs of the copper-containing MSS obtained are shown in Fig. 1. The individual spheres are of uniform appearance with an average diameter of about 180 nm. The relatively low temperature used for template removal during the synthesis of the spheres is undoubtedly favourable for preparation of a non-aggregated product. The more highly magnified image in Fig. 1b clearly displays the radial porosity of the silica frame. The TEM investigations did not provide

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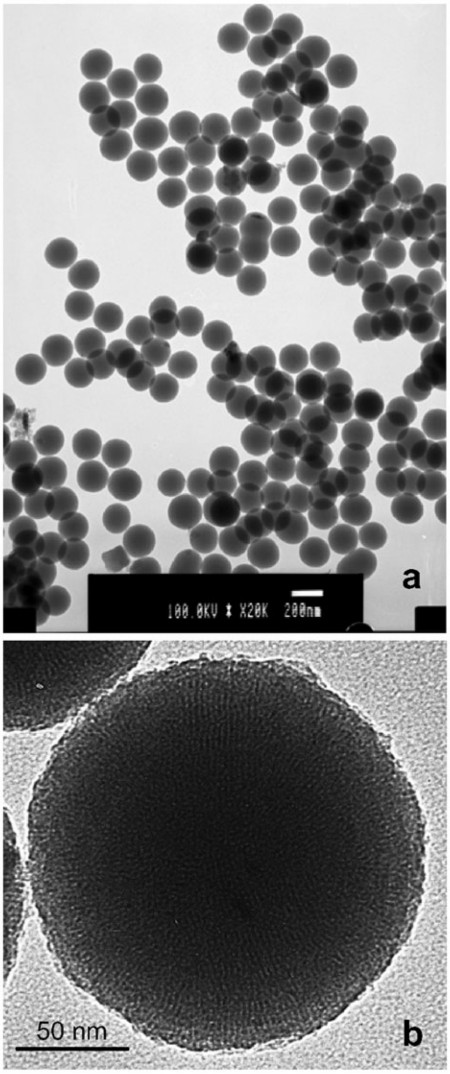

Fig. 1 TEM micrographs of copper-containing porous silica spheres: scale bar = 200 nm (a) and scale bar = 50 nm (b).

evidence for any nanometre-sized copper aggregate inside or outside the pore system. The nitrogen adsorption–desorption isotherm of the sample presented in Fig. 2 is typical of materials with pores in the small mesoporous size range. The specific surface area is 1260 $m^2\ g^{-1}$ and the pore volume is 0.66 mL g^{-1}. In the inset to Fig. 2 the pore size distribution calculated from the isotherm (BJH method) displays a narrow distribution with an average pore diameter around 2.3 nm, indicating that *in situ* incorporation of copper does not deteriorate the pore structure ordering of the material.

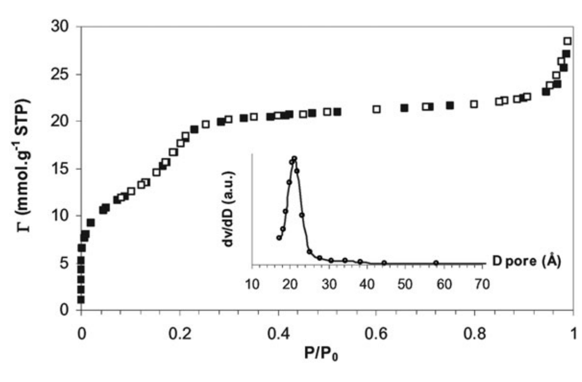

Fig. 2 Nitrogen adsorption (■) and desorption (□) isotherms at 77 K and pore size distribution (inset) of copper-containing porous silica spheres.

The copper loading in the material was determined to be 2 wt% using AAS. This metal content is a function of both the copper precursor concentration in the chloroform solution and the quantity of the organic phase solubilised in the micelles. The spherical shape of the particles is conserved for amounts of organic solution added up to the hydrophobic micellar volume calculated from the Tanford relation (calculation with an aggregation number of 50 units of DTAB per micelle), namely around 200 mL per mole of surfactant. The TPR profile acquired from the surface of copper-containing MSS is shown in Fig. 3. The reduction process is observed as a broad and asymmetric peak with a temperature at maximum reduction T_m around 212 °C. The hydrogen consumption peak in this region is assigned to the reduction of dispersed Cu(II) species to metallic copper. The T_m value of this reduction process is lower than the 300 °C reported for silica-supported CuO and agrees with those observed in previous TPR studies of copper-containing porous silica materials displaying comparable textural properties.[5,9] Taking into account the general dependence of T_m on the metal particle size, *i.e.* smaller particles are expected to be reduced at lower temperature, it can be inferred that copper species are located in a readily accessible position, dispersed at the pore surface. The nature and the location of the copper species have been further investigated using X-ray diffraction and DR UV–Vis spectroscopy (see ESI†). The results may be clearly interpreted as indicating that the Cu is located at the internal surface of the mesoporous silica spheres, mainly as mononuclear oxide species very well dispersed at the surface of the pores.[10] It can be concluded that using this pathway the metal remains located in the pores throughout the synthesis as expected, and is not partially mixed into the silica structure. This avoids any loss of its accessibility that commonly arises with direct incorporation methods. Indeed, as the metal precursor is solubilised in the surfactant micelle core, no interaction exists with the silica frame during the synthesis.

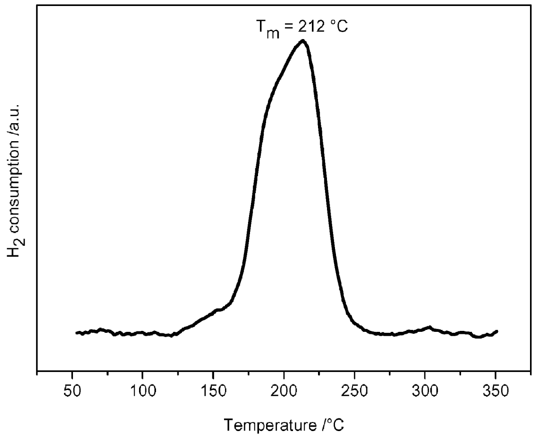

Fig. 3 H_2-TPR profile for copper-containing porous silica spheres.

In summary, a new one-step procedure has been described that allows the preparation of copper-containing monodisperse mesoporous silica spheres with perfect control of morphological and textural properties. It is possible to expect that higher loadings of metal in MSS can be achieved with no collapse of the porous architecture, as can occur by *in situ* metal incorporation.[5] Using the present preparation method, other metals can be likewise included in MSS for a wide range of applications, for example in catalysis or gas separation. Moreover, the size of the spheres can be tuned to meet the specific requirement of a given application.

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