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Large-scale synthesis of uniform silver orthophosphate colloidal nanocrystals exhibiting high visible light photocatalytic activity†

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Silver orthophosphate nanocrystals with controlled particle size have been synthesized using a simple, reproducible and easily scaled up route based on the reaction between silver ions, oleylamine and phosphoric acid. The obtained nanocrystals are highly uniform in size and exhibit high visible light activity for the photodecomposition of organic compounds.

Semiconductor-based photocatalysis is a promising avenue for solving many environmental and energy issues.¹ Developing suitable semiconductors serving as photocatalysts that efficiently employ sunlight as the energy source is thus one of the key objectives in material science.² Several visible light driven photocatalytic systems such as $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$,^{2a} $\text{TiO}_{2-x}\text{N}_x$,^{2b} and $\text{ZnS-CuInS}_2\text{-AgInS}_2$ ^{2d} have recently been developed. In this area, a breakthrough was made recently by Yi and co-workers, who reported the use of silver orthophosphate (Ag_3PO_4) as an active visible light photocatalyst for the oxidation of water and photodecomposition of organic compounds.³ These authors demonstrated that the photocatalytic activity of Ag_3PO_4 is far exceeding those of current known visible light photocatalysts *e.g.*, BiVO_4 or N-doped TiO_2 . However, the crystallite size of the Ag_3PO_4 remained relatively large (0.5–2 μm) which might actually limit the photocatalytic performance. To enhance photocatalytic activity of this new material, it is thus desirable to synthesize nanosized Ag_3PO_4 particles since surface-to-volume ratio and thus specific surface area increase dramatically as the particle size of a material decreases.⁴ Higher surface area of smaller particle size is expected to be beneficial for photocatalytic reactions which mostly occur on the surface the catalyst.⁵ In addition, the preparation of uniform Ag_3PO_4 particles in the nanometre range should also enable the study of structural, electronic and optical properties of this new material at the nanoscale.

Herein, we report for the first time a large-scale synthesis of uniform colloidal Ag_3PO_4 nanocrystals (NCs) with a precise

control of particle size ranging from 8 to 16 nm. This approach is based on simultaneous reaction of phosphoric acid (H_3PO_4) with silver ions (Ag^+) and oleylamine (OM) in an organic solvent at room temperature. The reaction between H_3PO_4 and Ag ions generates Ag_3PO_4 while the OM molecules are capping the surface of Ag_3PO_4 NCs through interaction between H_3PO_4 and OM. In the presence of OM, uniform OM-capped Ag_3PO_4 NCs are formed, which are soluble in nonpolar solvent. Most importantly, the surface of Ag_3PO_4 NCs can easily be modified, which in turn permits a tuning of surface hydrophobicity/hydrophilicity of these NCs (see ESI for experimental details†). Furthermore, this simple and reproducible approach can also be extended for the synthesis of several other metal phosphate colloidal NCs.

Transmission electron microscopy (TEM) images of the resulting Ag_3PO_4 NCs (Fig. 1A and B) show that the product consists of regularly shaped almost spherical NCs. Particle size analysis conducted by measuring cross diagonals of approximately 150 nanoparticles indicates an average size of 8.0 ± 0.6 nm. Selected area electron diffraction (SAED) image (Fig. 1D) reveals the crystalline nature of the sample, which is also confirmed by X-ray diffraction (XRD) as depicted in Fig. S1A†. The XRD pattern of the product exhibits well-defined peaks indicative of

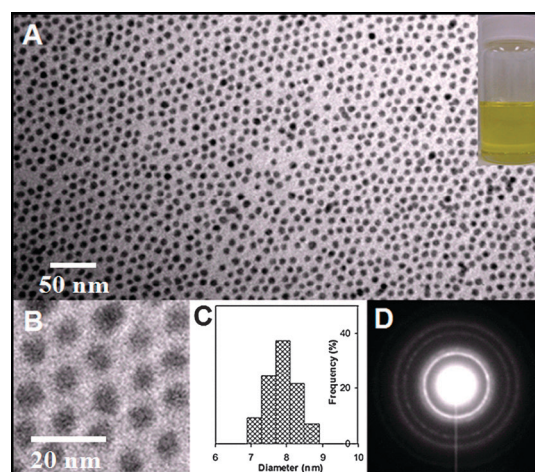


Fig. 1 TEM images of Ag_3PO_4 NCs: (A) low magnification and (B) high magnification; (Inset in A: photograph of Ag_3PO_4 NC dispersed in toluene). (C) Particle size distribution; (D) SAED of 8 nm Ag_3PO_4 NCs.

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highly crystalline Ag_3PO_4 with a body-centered cubic structure.^{3,6} UV-Vis absorption spectrum of the 8 nm Ag_3PO_4 NCs dispersed in toluene (Fig. S1B†) displays a strong light absorbance in the visible region. When plotting $(R/h\nu)^2$, *i.e.* the square of the absorption coefficient (R) multiplied by the photon energy ($h\nu$), versus $h\nu$ a direct band gap of 2.57 eV is obtained, while $(R/h\nu)^{1/2}$ versus $h\nu$ indicates an indirect band gap of 2.41 eV (Insets in Fig. S1B†). Both the direct band gap and the indirect band gap values of the thus-synthesized Ag_3PO_4 NCs are larger than those of micron-size Ag_3PO_4 particles (2.43 and 3.36 eV, respectively)³ which may due to size-dependent optical properties of semiconductors.^{4a,7}

The OM surfactant plays an important role in the formation of uniform Ag_3PO_4 NCs. To ascertain this point, an experiment was carried out in the absence of OM. As AgNO_3 does not dissolve in toluene, a small amount of an ethanol/water mixture was added to ensure total dissolution of AgNO_3 . When H_3PO_4 was added, a yellow precipitate of non uniform and large Ag_3PO_4 particles immediately formed (Fig. S2†). In contrast, in the presence of OM, AgNO_3 dissolved in toluene, the solution remaining transparent after the addition of H_3PO_4 . Acid–base interactions between OM and H_3PO_4 induce the formation of a layer of OM coating the Ag_3PO_4 NC surface. This OM layer, on one hand, protects the Ag_3PO_4 NCs from agglomeration by supplying the necessary repulsive force opposing the van der Waals attractions in between of NCs, and thus producing a clear solution. On the other hand, it hinders subsequent growth of Ag_3PO_4 crystals, maintaining the particles small and uniform. Fourier transform infrared (FTIR) spectroscopy was employed to confirm the presence of OM on the surface of Ag_3PO_4 NCs (Fig. 2A, curve (a)). Prior to performing these measurements, the samples were thoroughly washed to remove all unbound surfactant molecules. The two peaks at 2922 and 2852 cm^{-1} in the case of OM-capped Ag_3PO_4 NCs correspond to the asymmetric and symmetric stretching mode of methylene groups present in the alkyl chain of OM, while the peak at 2960 cm^{-1} is associated with the CH_3 stretching vibration.⁸

One important issue for the catalytic application of organic-capped NCs is removing the surfactant molecules from their surface. It is thus necessary to establish how the OM molecules are attached to the surface of Ag_3PO_4 NCs. To this end, we performed high resolution X-ray photoelectron spectroscopy (XPS) on the sample which had been thoroughly washed.

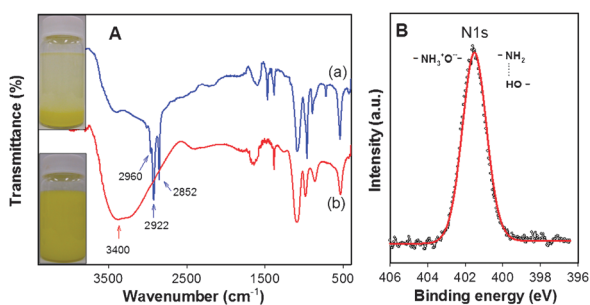


Fig. 2 FTIR spectra (A) of OM capped Ag_3PO_4 NCs before (a) and after (b) treatment with NH_4OH , and N1s XPS spectrum of the OM-capped Ag_3PO_4 NCs (B). Inset in A: photographs of the Ag_3PO_4 NCs in water before (upper) and after (lower) NH_4OH treatment.

As shown in Fig. 2B, the N1s XPS spectrum of OM-capped Ag_3PO_4 NCs exhibits only one peak at the binding energy of 401.5 eV which can be attributed to hydrogen-bonded or protonated nitrogen.⁹ This is of special interest because if OM molecules are indeed bonded to the Ag_3PO_4 NC surface through hydrogen-bonding interactions or proton exchange, OM may be displaced easily by other bases to allow the Ag_3PO_4 NCs surface to be re-functionalized differently. To verify this, we treated OM-capped Ag_3PO_4 NCs with ammonium hydroxide (NH_4OH) (see ESI†), and found that, after the NH_4OH treatment, Ag_3PO_4 NCs are well dispersed in water (Fig. 2A, lower inset) implying that the surface became hydrophilic upon this treatment. Note that, before treatment with NH_4OH , the hydrophobic Ag_3PO_4 NCs precipitated in polar solvents *e.g.*, ethanol or water (Fig. 2A, upper inset). FTIR performed on the NH_4OH -treated sample is depicted in Fig. 2A, curve (b). No FTIR peaks at 2922, 2852, and 2960 cm^{-1} , which would be characteristic of OM molecules capped on the surface of Ag_3PO_4 NCs, were observed indicating that all of the OM was fully removed from the surface of the Ag_3PO_4 NCs. In addition, a broad peak at around 3400 cm^{-1} indicates a large amount of water adsorbed on the surface and/or hydroxyl groups of Ag_3PO_4 NCs.^{8a,b} The XRD and TEM characterization performed on this sample, as shown in Fig. S3†, reveal no remarkable change in crystallinity and morphology upon this treatment. This result also confirms that, unlike other metal phosphate NCs synthesized using other types of surfactants, *e.g.* oleic acid, which strongly bond to the NC surface,¹⁰ the capping OM molecules on the Ag_3PO_4 NC surface are labile and can be displaced relatively easily. This feature is of great significance for photocatalytic applications as well as for further functionalization of the materials.

Our approach not only allows us to produce uniform Ag_3PO_4 NCs, but also it enables tuning of the size of these NCs. To prepare Ag_3PO_4 NCs with different crystallite sizes, a controlled amount of water was added to the synthesis mixture, as aqueous medium is known to favor the formation of large Ag_3PO_4 crystals.^{3,6} A series of experiments was performed by gradually increasing the amount of water added to the H_3PO_4 solution prior to addition to the Ag^+ solution. It was found that, with increasing the amount of water from 2.5 g to 5.0, 7.5, and 10.0 g, in the synthesis solution, the size of the resulting Ag_3PO_4 NCs progressively increased from 10 nm to 12 nm, 14 nm and then to 16 nm (Fig. 3A–D and S4–7†). When a larger amount of water was used (*e.g.*, 20.0 g), the formation of bigger (up to 40 nm) but less uniform Ag_3PO_4 NCs was observed (Fig. S8†). To explain this, the size of Ag_3PO_4 NCs might be governed by the relative rates of two reactions: (i) OM with H_3PO_4 and (ii) Ag ions with H_3PO_4 , which both depend on water content in the synthesis mixture. The former tends to induce small NCs while the latter favors growth of NCs. Increasing the water content in H_3PO_4 solution might enhance the affinity of this acid towards Ag ions, while its affinity to the organic OM is reduced. As a result, the reaction of Ag ions and H_3PO_4 would be faster, leading to the formation of larger NCs.

The photocatalytic activity of 8 nm Ag_3PO_4 NCs was evaluated by testing their ability to decompose methylene blue (MB) under visible light without using a sacrificial reagent

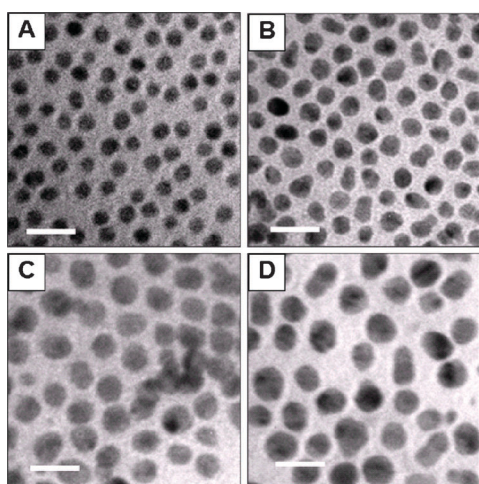


Fig. 3 TEM images of Ag_3PO_4 NCs with different sizes synthesized by varying the amount of water added to the H_3PO_4 solution: 2.5 g (A), 5.0 g (B), 7.5 g (C), and 10.0 g (D). All scale bars are 30 nm.

(see ESI†). The UV-Vis spectra and variation of MB concentration as a function of visible light irradiation are shown in Fig. S9† and Fig. 4, respectively. For comparison, the decomposition of MB over micron-sized Ag_3PO_4 particles (namely, Ag_3PO_4 MCs), N-doped TiO_2 -P25, commercial TiO_2 -P25, and in the absence of catalyst, under the same conditions are also shown (Fig. 4A). It is clearly seen that, both Ag_3PO_4 NCs and Ag_3PO_4 MPs showed superior catalytic activity in the photodecomposition of MB under visible light irradiation, as compared to those of N-doped TiO_2 -P25 and TiO_2 -P25. This can be explained by weak or essentially no absorption in the visible region for N-doped TiO_2 -P25 and TiO_2 -P25, respectively (Fig. S10†). In contrast, Ag_3PO_4 materials exhibit a strong absorption in the visible region, because of its smaller band gap (Fig. S10†). Moreover, compared to Ag_3PO_4 MCs, Ag_3PO_4 NCs showed a much higher photocatalytic performance. The photodecomposition rate constant (k) of MB over Ag_3PO_4 NCs, as calculated from a pseudo-first order reaction kinetic model: $\ln(C_0/C) = kt$, was 0.0294 min^{-1} , is double of that calculated for Ag_3PO_4 MCs (0.0141 min^{-1}). Furthermore, the amount of MB adsorbed on Ag_3PO_4 NCs after 60 min. of stirring in absence of light was 18.4% which was also twice as high as that adsorbed on Ag_3PO_4 MCs (9.1%).

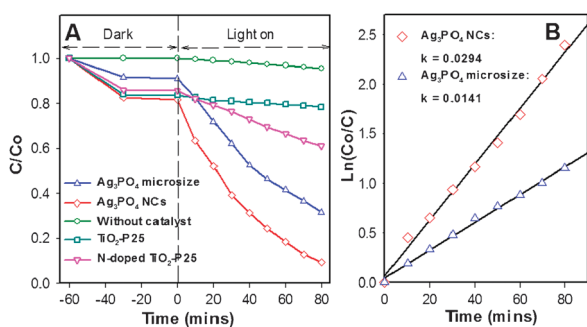


Fig. 4 Variation of MB concentration against irradiation time using Ag_3PO_4 NCs, Ag_3PO_4 MCs, N-doped TiO_2 -P25, TiO_2 -P25, and without catalyst, under visible light (A). Plots of $\ln(C_0/C)$ versus irradiation time representing the fit using a pseudo-first-order reaction rate (B).

Clearly, the specific surface area of Ag_3PO_4 NCs ($14.5 \text{ m}^2 \text{ g}^{-1}$) is much higher than that of Ag_3PO_4 MCs (less than $1 \text{ m}^2 \text{ g}^{-1}$). Therefore, the superior photocatalytic activity of Ag_3PO_4 NCs compared to those of larger Ag_3PO_4 particles can be attributed to the larger surface-to-volume ratio of the Ag_3PO_4 NCs.

Based on our approach, *e.g.*, simultaneous reactions of phosphoric H_3PO_4 with metal ions and OM in toluene, we were able to synthesize also other metal phosphate NCs such as calcium phosphate nanorods (Fig. S11†), lanthanum phosphate nanorods (Fig. S12†) and cerium phosphate nanoparticles (Fig. S13†). Further size and shape control of these materials is currently under way in our laboratory.

In summary, we have developed a simple and easily scalable approach for the fabrication of uniform Ag_3PO_4 NCs with controlled size in the range of 8 to 16 nm. The surface of surfactant-capped Ag_3PO_4 NCs can easily be modified, due to only weak interactions between OM molecules and the NC surface. Moreover, the new Ag_3PO_4 NCs, exhibit superior photocatalytic activity under visible light as compared to that of micron-sized Ag_3PO_4 particles, and it is much higher than those of N-doped TiO_2 -P25 and commercial TiO_2 -P25 materials. Our approach is a general method and can be extended to the synthesis of a variety of other colloidal metal phosphate NCs which have great potential applications in many other fields such as, for instance, biological sensors (calcium phosphate)¹¹ or luminescent devices (lanthanide phosphates).¹²

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