Photosynthesis and characterization of Prussian blue nanocubes on surfaces of Ti O 2 colloids

Yan-Yan Song, Ke Zhang, and Xing-Hua Xia

Articles you may be interested in

Experimental and molecular dynamics study of the growth of crystalline TiO2
J. Appl. Phys. **112**, 073527 (2012); 10.1063/1.4757010

The electronic and optical properties of Eu/Si-codoped anatase TiO2 photocatalyst
Appl. Phys. Lett. **100**, 102105 (2012); 10.1063/1.3692750

Relation between crystallinity and chemical nature of surface on wettability: A study on pulsed laser deposited TiO2 thin films
J. Appl. Phys. **109**, 123512 (2011); 10.1063/1.3594695

Visible light photocatalytic activity in nitrogen-doped TiO 2 nanobelts
Appl. Phys. Lett. **94**, 093101 (2009); 10.1063/1.3093820

Study on dark specific resistance of Au–TiO 2 nanogranular films
J. Vac. Sci. Technol. B **19**, 645 (2001); 10.1116/1.1366710

Photosynthesis and characterization of Prussian blue nanocubes on surfaces of TiO₂ colloids

Yan-Yan Song, Ke Zhang, and Xing-Hua Xia[a)]

Key Lab of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing 210093, China

Prussian blue (PB) nanocubes were synthesized on the surface of titania (TiO₂) colloids using two-step process with ultraviolet light illumination. The formation of PB nanocubes starts with its nucleation under strong ultraviolet light illumination and followed by a slow growth of the nuclei under low intensity natural light illumination. This kind of PB nanocube has a very low Curie temperature. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2169909]

Prussian blue (PB), formula $Fe_4^{III}[Fe^{II}(CN)_6]_3$, and its related metal hexacyanates have aroused intensive interest because of their potential application as molecule-based magnets. Many methods, including microemulsion,[1,2] polymer protection,[3] biomolecular matrix as a chemically and spatially confined environment,[4] have been advocated for the synthesis of PB and its analogs. Recently, deposition of ferromagnetic PB Langmuir films was reported.[5–9] We prepared compacted ultrathin PB films on electrode surfaces from an acidic ferricyanide solution.[10–12]

Titania (TiO₂) is the most studied semiconductor photocatalyst for various applications due to its high photocatalytic efficiency, chemical inertness, surface amphotericity, and nontoxicity. Photodeposition of metals such as Ag, Pt, and Pd on titania has been realized.[13–16] Reports on photosynthesis of materials other than metals are limited.[17–19] Tada *et al.*[17] and Uchicla[18] reported the photodeposition of PB film on TiO₂ but not cubic crystals since they used continuous strong ultraviolet light illumination. The unique magnetic behavior of PB depends on the constituents and ratios of the transition metal ions in the compound.[19–21] Here, we report on the photosynthesis of monodisperse PB nanocubes on surfaces of TiO₂ colloids by UV light irradiation of a TiO₂ suspension containing $FeCl_3$ and $K_3[Fe(CN)_6]$ for nucleation followed by weak intensity UV light illumination for crystal growth; thereby regular PB nanocubes are formed. The unique properties of the well-crystallized PB nanocubes were characterized.

For the photosynthesis of PB on TiO₂ colloids, equimolar amounts of aqueous $FeCl_3$ and $K_3[Fe(CN)_6]$ were mixed in the presence of 200 nm TiO₂ colloids [amorphous as indicated by the x-ray diffraction (XRD) pattern shown in Fig. 1, 5 mg/ml]. The suspension was purged with a stream of nitrogen for 15 min and then irradiated for 0.5 h using an indium lamp (250 W with the major emission wavelength at ~435 nm) for PB nucleation and followed by crystal growth under the sunlight illumination for 10 h at room temperature. The suspension was then centrifuged, and washed with deionized water three times to remove the supernatants. Transmission electron microscopy images of the air-dried sample revealed layers of regular PB nanocubes enwrapped the TiO₂ colloids [Figs. 1(a)–1(c)]. In our experiment, the

solution is weakly acidic, and the surface of TiO₂ colloid is positively charged. Therefore, ferricyanide anions adsorb on surfaces of TiO₂ colloids.[17,18] With illumination, electron of TiO₂ is excited to the conduction band, and subsequently driven to the surface of TiO₂ colloid under interior field. Although the thermodynamic potential of $Fe^{3+/2+}$ couple (0.771 V versus NHE) is higher than that for $Fe(CN)_6^{3-/4-}$ couple (0.356 V versus NHE), the excited electrons on the colloidal surface are preferential to reduce the adsorbed $Fe(CN)_6^{3-}$ anions to $Fe(CN)_6^{4-}$ which in turn couple with ferric ions in the solution leading to PB formation. The left holes in the valence band of TiO₂ also transfer to the surface resulting in the oxidation of H₂O to O₂.[17,18] Under illumination with UV light, PB nuclei are formed on the surface of TiO₂ colloids. Density of the PB nuclei is determined by the light intensity, illumination time, and the nature of TiO₂ phase.[22–24] Obviously, the growth process of the nuclei is important for the resulted PB structures. In our case, after the formation of PB nuclei under UV light illumination, we used natural light with much lower intensity to allow the slow growth of the PB nuclei. This process resulted in the growth of regular PB nanocrystals around the TiO₂ colloids [Figs. 2(a) and 2(b)]. All nanocrystals have regular cubic shape. High- resolution transmission electron microscopy (HR-TEM) image shows that the PB crystal has perfect nanocube form with a mean edge length of 40 nm. Electron diffraction
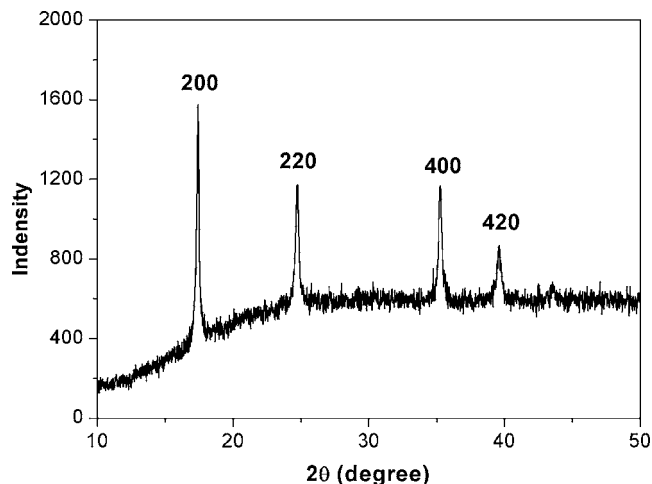

FIG. 1. XRD patterns of PB nanocubes deposited on surfaces of TiO₂ colloids.

[a)]Author to whom correspondence should be addressed; electronic mail: xhxia@nju.edu.cn
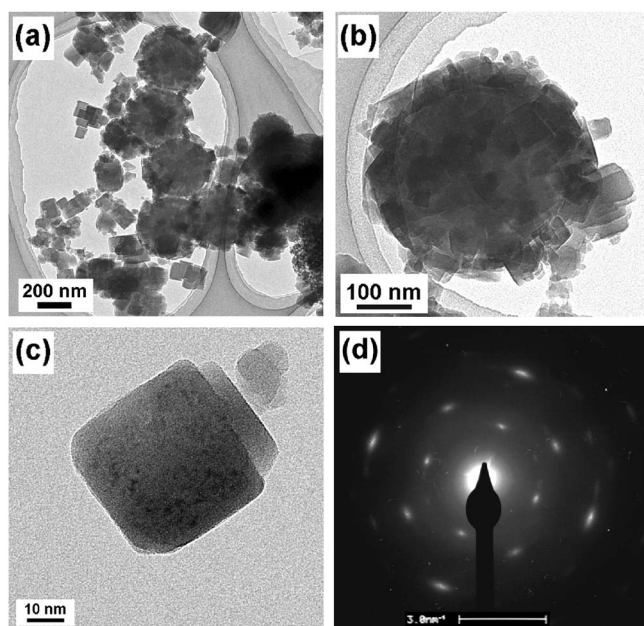
FIG. 2. TEM images of (a) and (b) TiO$_2$ colloid enwrapped by Prussian blue nanocubes, (c) HRTEM graph of Prussian blue nanocube, and (d) electron diffraction patterns of a single PB nanocube.
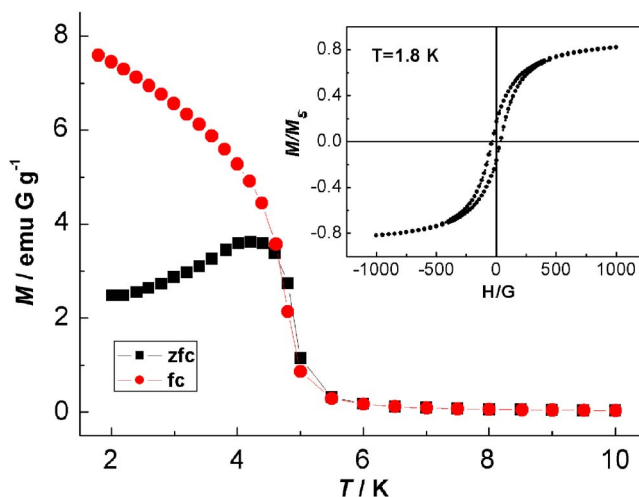

FIG. 3. (Color online) Field-cooled magnetization at 10 G as a function of temperature and hysteresis loop (inset) of the PB nanocubes deposited on surfaces of TiO$_2$ colloids.

(ED) pattern [Fig. 2(d)] of this single-crystal PB reveals a typical fcc structure of PB. The averaged d spacings measured from ED patterns from several measurements from different PB nanocubes (5.8 Å [200]; 4.0 Å [220]; 2.8 Å [400]; 2.1 Å [420]) are in agreement with the x-ray powder diffraction analysis. The TiO$_2$ used in our experiment is amorphous, as indicated by the XRD pattern (Fig. 1). The nature of TiO$_2$ phase (amorphous, anatase, and rutile) will affect the formation of small nuclei.[23,24] As we know, TiO$_2$ nanocrystallites with different crystal structures have different electron diffusion coefficients. The electron diffusion coefficient of the anatase TiO$_2$ is one order of magnitude larger than those of the rutile ones, and the electron diffusion coefficient of amorphous ones is the smallest, which means that the electron diffusion length of the amorphous TiO$_2$ is the shortest. Thus, the photogenerated electrons and holes will recombine more quickly than the others, resulting in fewer electron reaching the surface of TiO$_2$ colloids. In the first step of our method, compared with the anatase and rutile TiO$_2$, fewer PB nuclei will be formed on surfaces of amorphous TiO$_2$ colloids. For the same reason, the crystal growth of PB will certainly be affected in the second step. Therefore, we can expect that different morphology of PB will be formed on TiO$_2$ with different phase.

X-ray powder diffraction analysis was obtained by drying the precipitate on an indium tin oxide surface in the air (Fig. 2). It shows peaks at 17.6° (200), 24.9° (220), 35.5° (400), 39.8° (420), which can be indexed as the PB cubic space group $Fm3m$.[25] Infrared spectrum (not shown) of the sample exhibits a absorption band at 2088 cm^{-1} due to the CN stretching in the Fe^{2+}–CN–Fe^{3+} group of PB. The bands at 3443 and 1634 cm^{-1} are due to the O–H stretching and H–O–H bending modes, respectively, indicating the presence of interstitial water in the compound.[10–12,26]

The fcc structure of PB allows three-dimensional long-range superexchange interactions between the neighboring Fe^{3+} ions ($S=5/2$) through the NC–Fe–CN linkages, leading to a ferromagnetic ordering property at low temperature.[25–27]

The magnetic properties of the resulted nanocubes using two-step photosynthesis method were investigated by a magnetic property measurement system (Quantum Design MPMS-XL, USA). The magnetic response of the PB nanocubes on surfaces of TiO$_2$ colloids was measured as a function of temperature and applied field. The field-cooled (FC) magnetization versus temperature of PB nanocubes at $H=10$ G shows a break at $T_C=4.6$ K [the crossing point of M_{fc} and M_{zfc}, Fig. 3 (zfc=zero field cooled)] that is lower than in the bulk materials (5.6 K).[27–29] For PB analogs, Curie temperature T_C is expressed as[30]

$$T_c = \frac{2\sqrt{Z_{ij}Z_{ji}}|J_{ij}|}{3k_B}\sqrt{S_i(S_i+1)S_j(S_j+1)}, \quad (1)$$

where $i=j=$Fe^{3+}, $S_i=S_j=5/2$, Z_{ij} or Z_{iij} is the number of the nearest-neighbor $i(j)$-site ions surrounding a $j(i)$-site ion. k_B is the Boltzmann constant, and J is the magnetic interaction constant. As the lattice parameter of nanocrystals does not change, we suppose that the magnetic interaction constant J_{ij} between the Fe^{3+} ions of PB nanocubes is almost the same as that of bulk. Therefore, the decrease in the Curie temperature T_C of the PB nanocubes is perhaps due to the diminution of the average number of nearest magnetic interaction neighbors in PB nanocubes with perfect crystal structure. Besides, defects could be present on the surface or internal of the Prussian blue cubes, which may effect the T_C. A clear hysteresis loop of the nanocubes is observed in the field-dependent magnetization at $T=1.8$ K, with a coercive field (H_c) of 67 G (inset in Fig. 3). This behavior is similar to PB bulk obtained from neutron scattering measurement.[31] Our results demonstrate that the PB nanocubes are magnetic molecular crystals.

In conclusion, we report on the photosynthesis of PB nanocubes on surfaces of TiO$_2$ colloids in an aqueous solution of ferric-ferricyanide solution at room temperature and under ambient pressure, in which PB nuclei on TiO$_2$ surfaces were formed using strong UV light illumination followed by a slow growth process using low intensity natural light illumination. The resulted PB nanocubes are regular in size and highly crystal with a fcc structure. The observed decrease in the Curie temperature demonstrates the average number of magnetic interaction neighbors is limited due to its perfected

structure. The ion-selective properties, battery applications of the formed Prussian blue nanocubes, will be studied in the near future.

[1] S. Vaucher, M. Li, and S. Mann, Angew. Chem., Int. Ed. **39**, 1793 (2000).

[2] S. Vaucher, J. Fielden, M. Li, E. Dujardin, and S. Mann, Nano Lett. **2**, 225 (2002).

[3] T. Uemura and S. Kitagawa, J. Am. Chem. Soc. **125**, 7814 (2003).

[4] J. M. Dominguez-Vera and E. Colacio, Inorg. Chem. **42**, 6983 (2003).

[5] C. Mingotaud, C. Lafuente, J. Amiell, and P. Delhaes, Langmuir **15**, 289 (1999).

[6] S. Choudhury, N. Bagkar, G. K. Dey, H. Subramanian, and J. V. Yakhmi, Langmuir **18**, 7409 (2002).

[7] C. T. Black, C. B. Murray, R. L. Sandstrom, and S. Sun, Science **290**, 1131 (2000).

[8] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, Science **287**, 1989 (2000).

[9] S. Hashimoto, A. Maesaka, K. Fujimoto, and K. Bessho, J. Magn. Magn. Mater. **121**, 471 (1993).

[10] D. Zhang, K. Zhang, Y. L. Yao, X. H. Xia, and H. Y. Chen, Langmuir **20**, 7303 (2004).

[11] D. Zhang, K. Wang, D. C. Sun, X. H. Xia, and H. Y. Chen, Chem. Mater. **15**, 4163 (2004).

[12] Y. Zhang, Y. Wen, Y. Liu, D. Li, and J. H. Li, Electrochem. Commun. **6**, 1180 (2004).

[13] B. Kraeuther and A. J. Bard, J. Am. Chem. Soc. **100**, 4317 (1978).

[14] H. Reiche, W. W. Dunn, and A. J. Bard, J. Phys. C **83**, 2248 (1979).

[15] F. Zhang, N. Guan, Y. Li, X. Zhang, J. Chen, and H. Zeng, Langmuir **19**, 8230 (2003).

[16] F. Zhang, J. Chen, X. Zhang, W. Gao, R. Jin, N. Guan, and Y. Li, Langmuir **20**, 9329 (2004).

[17] H. Tada, Y. Saito, and H. Kawahara, J. Electrochem. Soc. **138**, 140 (1991).

[18] H. Uchicla, T. Sasski, and K. Ogura, J. Mol. Catal. **93**, 269 (1994).

[19] S. Ohkoshi, Y. Abe, A. Fujishima, and K. Hashimoto, Phys. Rev. Lett. **82**, 1285 (1999).

[20] S. Ferlay, T. Mallah, R. Quahe's, P. Veillet, and M. Verdaguer, Nature (London) **378**, 701 (1995).

[21] H. S. Holmes and G. S. Girolami, J. Am. Chem. Soc. **121**, 5593 (1999).

[22] S. Kambe, S. Nakade, Y. Wada, T. Kitamura, and S. Yanagida, J. Mater. Chem. **12**, 723 (2002).

[23] H. Tada, S. Tsuji, and S. Ito, J. Colloid Interface Sci. **239**, 196 (2001).

[24] N. R. Tacconi, K. Rajeshwar, and R. O. Lezna, Electrochim. Acta **45**, 3403 (2000).

[25] H. J. Buser, D. Schwarzenbach, W. Petter, and A. Ludi, Inorg. Chem. **16**, 2704 (1977).

[26] K. Itaya, I. Uchida, and V. D. Neff, Acc. Chem. Res. **19**, 162 (1986).

[27] A. Ito, M. Suenaga, and K. J. Ono, Chem. Phys. **48**, 3597 (1968).

[28] E. Dujardin and S. Mann, Adv. Mater. (Weinheim, Ger.) **16**, 1125 (2004).

[29] P. H. Zhuo, D. S. Xue, H. Q. Luo, and X. G. Chen, Nano Lett. **2**, 845 (2002).

[30] S. Ohkoshi, T. Iyoda, A. Fujishima, and K. Hashimoto, Phys. Rev. B **56**, 11642 (1997).

[31] F. Herren, P. Fischer, A. Ludi, and W. Halg, Inorg. Chem. **19**, 956 (1980).