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Research Article

Photocatalytically Active $YBa_2Cu_3O_{7-x}$ Nanoparticles Synthesized via a Soft Chemical Route

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$YBa_2Cu_3O_{7-x}$ (YBCO) nanoparticles (NPs) were synthesized via a soft chemical approach and they were found photocatalytically active at room temperature. Using metal acetate as precursors, a well-designed soft chemical procedure was carried out to produce YBCO NPs. The very small particle size and/or large number of defects might have led the NPs to semiconductors with vigorous photocatalytic activities. This work provides a direct and efficient route to obtain multifunction in YBCO based nanomaterials which are based on specific size and surface effects.

1. Introduction

High temperature superconductivity has been one of the most important chapters in the field of solid-state physics since it was discovered in 1986 [1]. As one of the most important high-Tc oxide superconductors, $YBa_2Cu_3O_{7-x}$ (YBCO) owns a well-defined cation stoichiometry and is easy to synthesize [2]. Research related to YBCO physical and chemical properties has been reported in a great number of publications [3–5].

Along with industrial advance, environmental issues such as the remediation of hazardous waste, contaminated ground-waters, and control of toxic air contaminant have arisen [6]. Photocatalysis by polycrystalline semiconductor oxides is a way to degrade organic and inorganic pollutants [7]. Many semiconductor materials have been investigated and used because of their photodegradation properties [8]. One of the most famous photocatalysts is TiO_2, which has showed excellent photocatalytic effect as reported [9–15]. Meanwhile, doped TiO_2 and many other complex oxides were also investigated for their photocatalytic properties [16–19]. As mentioned in the literature, the superconductivity of YBCO can be derived from its unique structure [20–22]. The distortion of Cu-O crystal plane caused by a certain amount of oxygen deficiency plays a significant role in superconductivity [23]. However, in some structure modified cases, the normal crystal structure related to superconductivity may be changed, resulting in nonsuperconductivity of YBCO materials (which may eventually transform to the semiconductor) [24, 25]. It is known that the fixed band gap in a semiconductor is the origin of its photocatalysis. Besides, nanosize single crystal may also exhibit different characteristics with traditional materials because of its special structure and size [4, 26–32]. In this case, YBCO may have photocatalytic activities. Although the electrical properties of YBCO have been investigated thoroughly and extensively, few studies if any on photocatalytic activities of YBCO materials have been reported up until now.

As a conventional synthesis technique, soft chemical method has potential to be applied for large-scale preparation on account of many factors: simple instruments, controllable procedures, cheap original chemicals, and high dimension uniformity [33–35]. In this work, YBCO nanoparticles (NPs) were synthesized through soft chemical method. In addition to conventional structure measurements, the photocatalytic

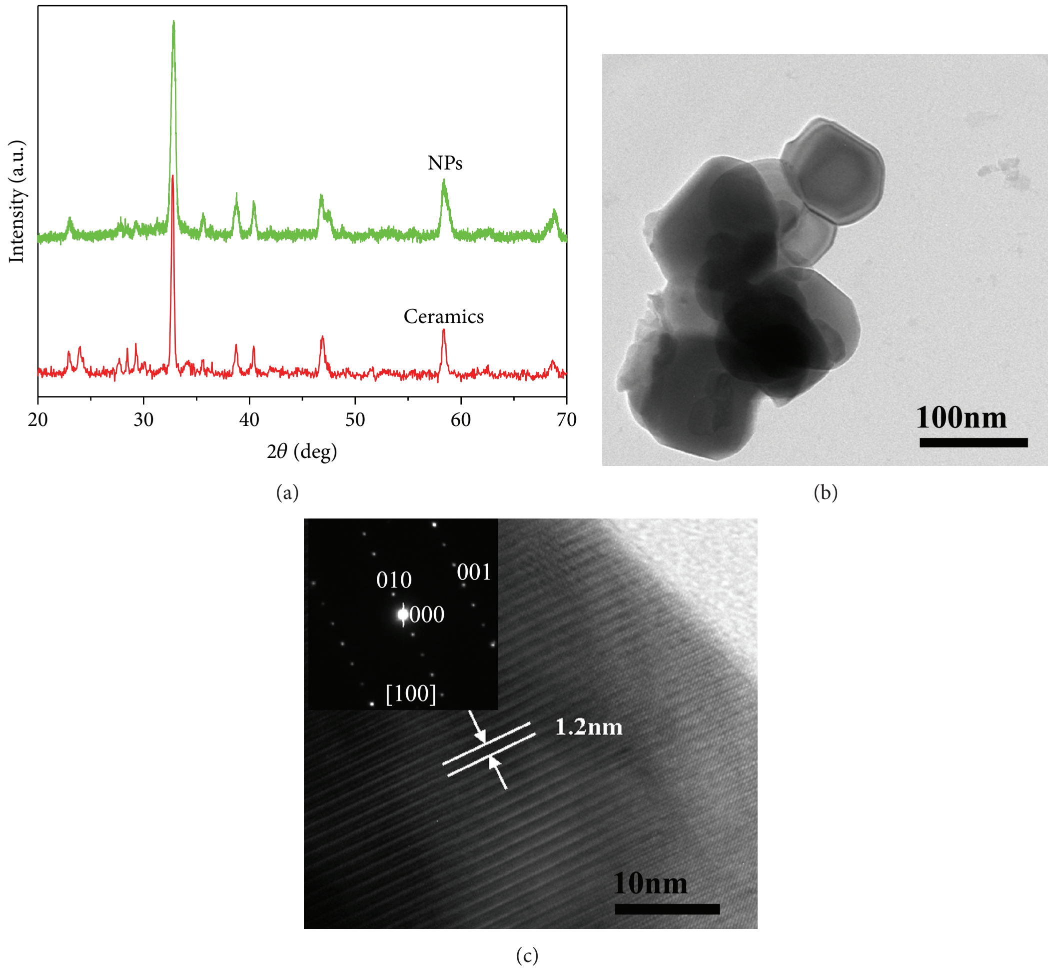

Figure 1: (a) XRD patterns of YBCO NPs (NPs, green line) and corresponding ceramics (red line) sintering at 900°C for 2 h. (b) TEM image of YBCO NPs. (c) HRTEM image of YBCO NPs, inset: the SAED pattern.

properties of YBCO NPs and YBCO ceramics were systematically investigated. The superconductivity of the YBCO ceramics was also studied for comparison.

2. Experimental Methods

$YBa_2Cu_3O_{7-x}$ NPs were synthesized from precursors $Y(CH_3COO)_3 \cdot 4H_2O$, $Ba(CH_3COO)_2$ and $Cu(CH_3COO)_2 \cdot H_2O$ with stoichiometric ratio of 1 : 2 : 3. The pH value of the stable solution was adjusted to 1~2 by adding certain amount of aqueous ammonia ($NH_3 \cdot H_2O$) and nitric acid (HNO_3). After annealing in flowing oxygen environment at 900°C for 2 hours, black YBCO NPs powders were obtained. Furthermore, YBCO ceramics were prepared through conventional process using YBCO NPs as precursors. The pellet was sintered in flowing oxygen environment at 900°C for 2 hours. In the photocatalytic measurement, YBCO NPs were dispersed in methylene blue (MB) with certain concentration, and the ceramics were grinded into powders as contrast.

Phase structures of the final samples were studied on a Philips X-ray diffraction (XRD) system using CuKα (λ = 1.5406 Å) as the radiation source. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained through a JEOL 2011 transmission electron microscope at an acceleration voltage of 200 kV. The superconducting transition temperatures were measured by Closed Cycle Refrigerator System. The UV absorption spectra were measured using a Shimadzu UV-2550 (Kyoto, Japan) spectrophotometer. Photocatalytic activities of the NPs for degradation of MB were evaluated by agitating the solution and irradiating the samples using a 250 W high-pressure Hg lamp. The initial concentration of MB was 1.8×10^{-5} mg/L with a catalyst loading of 1.5×10^{-3} mol/L in the experiment.

3. Results and Discussion

XRD patterns of as-synthesized YBCO NPs and ceramics are shown in Figure 1(a). It can be seen that the diffraction peaks correspond to pure-phase YBCO, which has a perovskite structure with an orthorhombic symmetry. In our case, pure-phase and higher crystallized YBCO NPs could be formed by using chelate compound as precursor, which can function

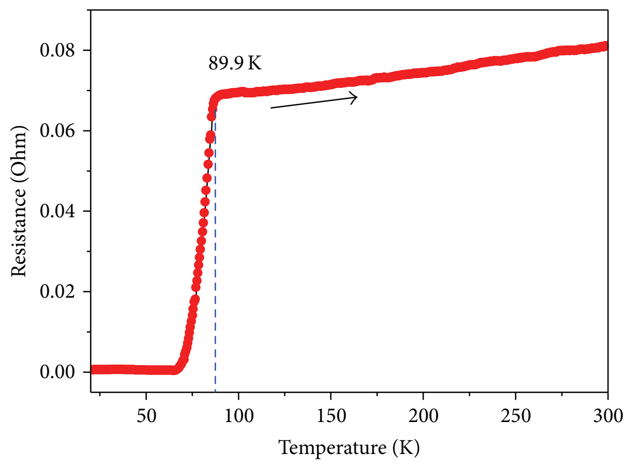

FIGURE 2: Resistance-temperature curve of YBCO ceramics sample.

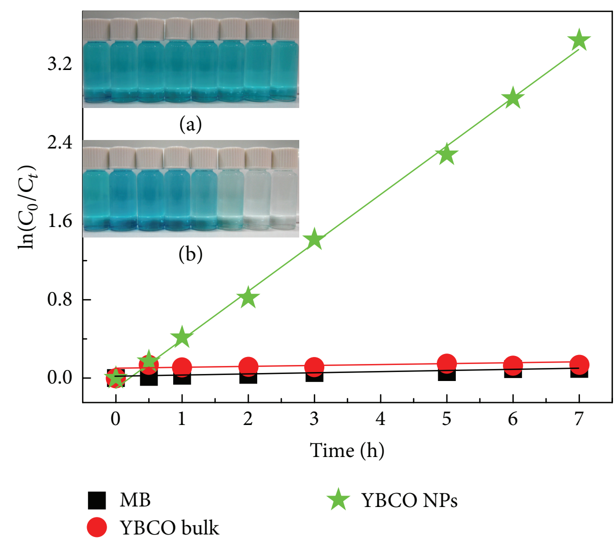

FIGURE 3: Photodegradation of MB solution with different photocatalysts: no catalysts (black line), YBCO ceramics (red line), and YBCO NPs (green line). Inset (a) MB solution using YBCO ceramics powders as photocatalyst after different hours of irradiation. Inset (b) MB solution using YBCO NPs as photocatalyst after different hours of irradiation.

stably in a strong acid environment with pH value 1~2. Further structure characterizations of YBCO NPs were made using TEM as shown in Figures 1(b) and 1(c). One can see that the YBCO NPs have an average diameter of about 100 nm. Figure 1(c) shows the HRTEM image and SAED pattern of the sample. As presented, the NPs are highly crystallized with a lattice spacing of about 1.2 nm, corresponding to interlayer spacing of the (010) planes in the YBCO crystal lattice.

To prove the superconductivity of YBCO ceramics synthesized from YBCO NPs, the conducting properties of the samples were determined. The resistance versus temperature curve in Figure 2 clearly shows that the YBCO ceramics exhibited behaviour of a typical high-Tc superconductor. It has transition temperature width from onset temperature 89.9 K to zero-resistance temperature 64.9 K.

The photocatalytic activities of YBCO NPs and ceramics powders were evaluated by the decomposition of methylene blue (MB) under the irradiation of a medium-pressure Hg lamp. A group of MB solution with no catalysts was also treated as contrast. In the literature, MB is usually used as standard dyes in photocatalytic activity testing for its photostability. Figure 3 shows the photodegradation of MB solution as a function of reaction time for different catalysts. In the photocatalysis measurement, we took groups of photodegraded solution several times and then used the spectrophotometer to measure the UV adsorption spectra. C_0 and C_t represent the intensity of the maximum absorption peaks of the UV adsorption spectra of solution initially and at time t. Take nature logarithm function of ratio C_0/C_t to obtain the ordinate in Figure 3. It can be seen that MB solution without catalyst is stable under irradiation. This phenomenon was also found when the YBCO ceramic powders were used as photocatalyst. However, in the presence of YBCO NPs, the MB concentration dropped to almost zero after 7 hours of irradiation. Such remarkable contrast could also be observed in the insets ((a) and (b)) in Figure 3. The colour of MB solution using YBCO ceramics powders as photocatalyst shows no changes during the 7-hour irradiation. On the other hand, almost all dyes in the MB solution which carried YBCO NPs were degraded after 7 hours. Therefore it can be concluded that YBCO NPs and corresponding ceramics behaved significantly different in photocatalysis.

Previous studies suggested that an appropriate band-gap in semiconductor catalysts is the origin of its photocatalytic activities. In photocatalysis, when the energy irradiation is higher or equal to the band-gap of the semiconductor catalyst, excited state valence-band holes and conduction-band electrons would form [6–8]. Then the holes and electrons could be got trapped in metastable surface states to recombine or react with electron acceptors and electron donors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. If a suitable scavenger or surface defect state is available to trap the electrons or holes, the recombination could be prevented. Subsequently, the holes and electrons generated by exciting photons could have redox reaction with dyes in the solutions. It means that suitable band-gap energy is a key reason in photocatalysis. Therefore, photocatalysis cannot take place in conductors and/or superconductors. From the resistance versus temperature curve (Figure 2), it is evident that YBCO ceramics fabricated from NPs show superconductivity. So YBCO ceramics could not lead to photodegradation of MB.

However, for the YBCO NPs, they show significant photodegradation. As discussed above, surface defects were also another important reason in photocatalysis for the excited state valence-band holes and conduction-band electrons were trapped in metastable surface states in the reaction. Generally speaking, it is easy to attribute this abnormal photocatalysis to very small particle size (and/or large number of defects). But their TEM images in Figure 1(b) reveal the nanoparticle size is about 100 nm, which is relatively large and the surface atoms are not enough to dominate this novel property. So the main reason for this phenomenon must come from modified band-gap energy in YBCO NPs.

As a famous high temperature superconductor, YBCO also has different conductivities depending on its oxygen content. Researches showed that $YBa_2Cu_3O_{7-x}$ had a semiconductor-like resistance characteristic when its oxygen content is in the range $0.5 < x < 0.7$ [36, 37]. Besides, for YBCO NPs in this work, it has single crystal phase as shown in Figure 1(c). Under the action of many mechanisms, YBCO single crystal can also perform novel properties [28–31], such as the formation of oxygen vacancies clusters [32]. Moreover, as compared to our former researches on the high temperature superconductor YBCO [5], the annealing period for YBCO NPs is relatively shorter in this work. So the oxygen content of YBCO NPs could be dominated by both the single crystal and the shorter annealing period. As a result, these might have led the YBCO NPs to be nonsuperconductive and have proper band-gap energy, which consequently make it possible to exhibit the vigorous photocatalytic activities. As a matter of fact, there are reports in the literature that, in some structure modified cases, the superconductivity of YBCO materials has vanished, which is likely to be consistent with our samples [20, 23]. This could be an effective method to investigate the potential properties and application in YBCO based composites. More characterization (such as PL spectra) and detailed study on the novel properties of YBCO NPs are highly desired [38].

4. Conclusions

YBCO NPs with narrow size distribution were obtained through a soft chemical route. The results showed that YBCO nanoparticles could produce excellent photocatalytic effects, while no degradation reactivities were observed for YBCO ceramics with normal superconductivity. The semiconductive nature induced by structure modification may be accounted for the photocatalytic effect of YBCO nanoparticles.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

Authors' Contribution

Zhenjiang Shen and Yongming Hu contributed equally to this work.

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References

[1] G. Blatter, M. V. Feigelman, V. B. Geshkenbein, A. I. Larkin, and V. M. Vinokur, "Vortices in high-temperature superconductors," *Reviews of Modern Physics*, vol. 66, no. 4, pp. 1125–1388, 1994.

[2] R. X. Liang, P. Dosanjh, D. A. Bonn, D. J. Baar, J. F. Carolan, and W. N. Hardy, "Growth and properties of superconducting YBCO single crystals," *Physica C*, vol. 195, no. 1-2, pp. 51–58, 1992.

[3] M. A. Beno, L. Soderholm, D. W. Capone et al., "Structure of the single-phase high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$," *Applied Physics Letters*, vol. 51, no. 1, pp. 57–59, 1987.

[4] D. A. Wollman, D. J. van Harlingen, W. C. Lee, D. M. Ginsberg, and A. J. Leggett, "Experimental determination of the superconducting pairing state in YBCO from the phase coherence of YBCO-Pb dc SQUIDs," *Physical Review Letters*, vol. 71, no. 13, pp. 2134–2137, 1993.

[5] Z. J. Shen, Y. Wang, W. P. Chen et al., "Electrospinning preparation and high-temperature superconductivity of $YBa_2Cu_3O_{7-x}$ nanotubes," *Journal of Materials Science*, vol. 48, no. 11, pp. 3985–3990, 2013.

[6] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.

[7] G. Palmisano, V. Augugliaro, M. Pagliaro, and L. Palmisano, "Photocatalysis: a promising route for 21st century organic chemistry," *Chemical Communications*, no. 33, pp. 3425–3437, 2007.

[8] A. Mills and S. Le Hunte, "An overview of semiconductor photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 108, no. 1, pp. 1–35, 1997.

[9] S. Livraghi, A. Votta, M. C. Paganini, and E. Giamello, "The nature of paramagnetic species in nitrogen doped TiO_2 active in visible light photocatalysis," *Chemical Communications*, vol. 28, no. 4, pp. 498–500, 2005.

[10] S. M. Fonseca, A. L. Barker, S. Ahmed, T. J. Kemp, and P. R. Unwin, "Direct observation of oxygen depletion and product formation during photocatalysis at a TiO_2 surface using scanning electrochemical microscopy," *Chemical Communications*, vol. 9, no. 8, pp. 1002–1003, 2003.

[11] T. L. Thompson and J. T. Yates Jr., "TiO_2-based photocatalysis: surface defects, oxygen and charge transfer," *Topics in Catalysis*, vol. 35, no. 3-4, pp. 197–210, 2005.

[12] A. L. Linsebigler, G. Lu, and J. T. Yates Jr., "Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.

[13] J. Zhang, L. S. Qian, W. Fu, J. H. Xi, and Z. G. Ji, "Alkaline-earth metal Ca and N codoped TiO_2 with exposed {001} facets for enhancing visible light photocatalytic activity," *Journal of the American Ceramic Society*, vol. 97, no. 8, pp. 2615–2622, 2014.

[14] J. Zhang, W. K. Chen, J. H. Xi, and Z. G. Ji, "{001} Facets of anatase TiO_2 show high photocatalytic selectivity," *Materials Letters*, vol. 79, pp. 259–262, 2012.

[15] J. Zhang, W. Fu, J. H. Xi et al., "N-doped rutile TiO_2 nano-rods show tunable photocatalytic selectivity," *Journal of Alloys and Compounds*, vol. 575, pp. 40–47, 2013.

[16] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science*, vol. 293, no. 5528, pp. 269–271, 2001.

[17] Y.-M. Hu, H.-S. Gu, D. Zhou, Z. Wang, H. L.-W. Chan, and Y. Wang, "Orientation-control synthesis of $KTa_{0.25}Nb_{0.75}O_3$

nanorods," *Journal of the American Ceramic Society*, vol. 93, no. 3, pp. 609–613, 2010.

[18] O. Carp, C. L. Huisman, and A. Reller, "Photoinduced reactivity of titanium dioxide," *Progress in Solid State Chemistry*, vol. 32, no. 1-2, pp. 33–177, 2004.

[19] S. Ould-Chikh, O. Proux, P. Afanasiev et al., "Photocatalysis with chromium-doped TiO_2: bulk and surface doping," *ChemSusChem*, vol. 7, no. 5, pp. 1361–1371, 2014.

[20] R. J. Cava, A. W. Hewat, E. A. Hewat et al., "Structural anomalies, oxygen ordering and superconductivity in oxygen deficient $Ba_2YCu_3O_x$," *Physica C: Superconductivity and its applications*, vol. 165, no. 5-6, pp. 419–433, 1990.

[21] P. X. Zhang and H.-U. Habermeier, "Atomic layer thermopile materials: physics and application," *Journal of Nanomaterials*, vol. 2008, Article ID 329601, 12 pages, 2008.

[22] H. I. Wang, W. T. Tang, L. W. Liao et al., "Femtosecond laser-induced formation of wurtzite phase ZnSe nanoparticles in air," *Journal of Nanomaterials*, vol. 2012, Article ID 278364, 6 pages, 2012.

[23] J. D. Jorgensen, B. W. Veal, A. P. Paulikas et al., "Structural properties of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$," *Physical Review B*, vol. 41, no. 4, pp. 1863–1877, 1990.

[24] S. Linzen, J. Kräußlich, A. Köhler, P. Seidel, B. Freitag, and W. Mader, "Unusual crystal structure of non-superconducting $Y_1Ba_2Cu_3O_{7-x}$ films on buffered silicon substrates," *Physica C: Superconductivity and Its Applications*, vol. 290, no. 3-4, pp. 323–333, 1997.

[25] M. Longhin, A. J. Kreisler, and A. F. Dégardin, "Semiconducting YBCO thin films for uncooled terahertz imagers," *Materials Science Forum*, vol. 587-588, pp. 273–277, 2008.

[26] C. Lin, X. Zhu, J. Feng et al., "Hydrogen-incorporated TiS_2 ultrathin nanosheets with ultrahigh conductivity for stamp-transferrable electrodes," *Journal of the American Chemical Society*, vol. 135, no. 13, pp. 5144–5151, 2013.

[27] Y. Q. Guo, K. Xu, C. Z. Wu, J. Y. Zhao, and Y. Xie, "Surface chemical-modification for engineering the intrinsic physical properties of inorganic two-dimensional nanomaterials," *Chemical Society Reviews*, vol. 44, no. 3, pp. 637–646, 2015.

[28] K. Xu, X. L. Li, P. Z. Chen et al., "Hydrogen dangling bonds induce ferromagnetism in two-dimensional metal-free graphitic-C_3N_4 nanosheets," *Chemical Science*, vol. 6, no. 1, pp. 283–287, 2015.

[29] R. Liang, D. A. Bonn, and W. N. Hardy, "Discontinuity of reversible magnetization in untwinned YBCO single crystals at the first order vortex melting transition," *Physical Review Letters*, vol. 76, no. 5, pp. 835–838, 1996.

[30] J. Y. T. Wei, N.-C. Yeh, D. F. Garrigus, and M. Strasik, "Directional tunneling and andreev reflection on $YBa_2Cu_3O_{7-\delta}$ single crystals: predominance of d-wave pairing symmetry verified with the generalized blonder, tinkham, and klapwijk theory," *Physical Review Letters*, vol. 81, no. 12, pp. 2542–2545, 1998.

[31] F. M. Sauerzopf, "Anisotropic flux pinning in $YB_{a2}Cu_3O_{7-\delta}$ single crystals: the influence of defect size and density as determined from neutron irradiation," *Physical Review B—Condensed Matter and Materials Physics*, vol. 57, no. 17, pp. 10959–10971, 1998.

[32] D. A. Lotnyk, A. V. Bondarenko, A. A. Zavgorodniy, M. A. Obolenskiy, and A. Feher, "Anisotropy of static and dynamic order-disorder transition in $YBa_2Cu_3O_{7-\delta}$ single crystal," *Journal of Physics: Conference Series*, vol. 150, no. 5, Article ID 052142, 2009.

[33] Z. Chen, Q. Gao, C. Wu, M. Ruan, and J. Shi, "Preparation and properties of an ordered, uniform 0.9 nm Ag array assembled in a nanoporous VSB-1 by a simple soft chemical method," *Chemical Communications*, vol. 10, no. 17, pp. 1998–1999, 2004.

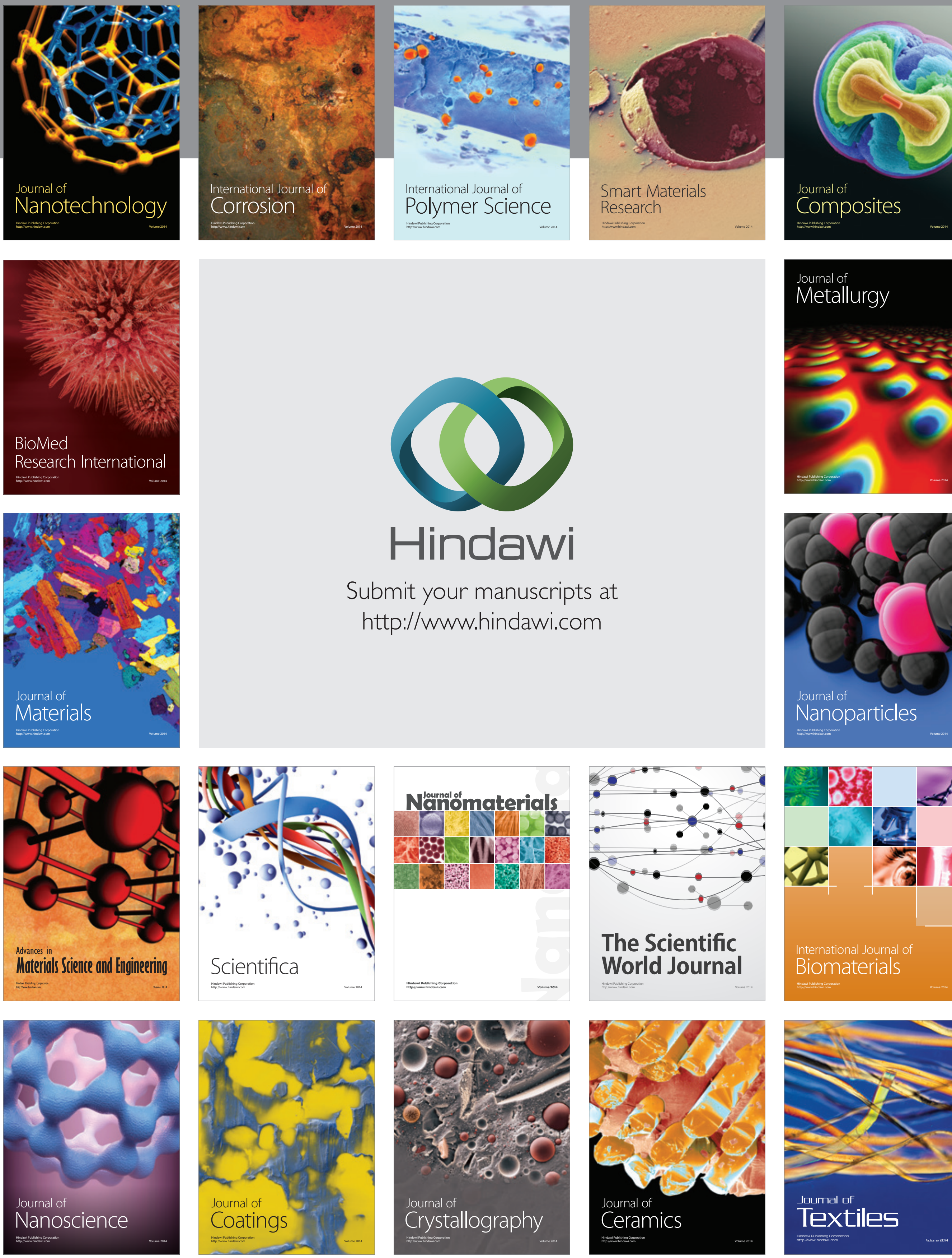
[34] N. R. Jana, L. Gearheart, and C. J. Murphy, "Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio," *Chemical Communications*, no. 7, pp. 617–618, 2001.

[35] W. Z. Wang and L. Ao, "A soft chemical synthesis of TiO_2 nanobelts," *Materials Letters*, vol. 64, no. 8, pp. 912–914, 2010.

[36] M. Longhin, A. J. Kreisler, and A. F. Dégardin, "Semiconducting YBCO thin films for uncooled terahertz imagers," *Materials Science Forum*, vol. 587-588, pp. 273–277, 2008.

[37] V. S. Jagtap, A. Scheuring, M. Longhin, A. J. Kreisler, and A. F. Dégardin, "From superconducting to semiconducting YBCO thin film bolometers: sensitivity and crosstalk investigations for future thz imagers," *IEEE Transactions on Applied Superconductivity*, vol. 19, no. 3, pp. 287–292, 2009.

[38] X. Peng, L. Manna, W. Yang et al., "Shape control of CdSe nanocrystals," *Nature*, vol. 404, no. 6773, pp. 59–61, 2000.



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