Synthesis, characterization and application of superhydrophobic low-cost Cu and Al nanoparticles

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Abstract

Cu and Al nanoparticles were prepared using a simple chemical etching method followed by a chemical reduction method. The synthesized metal nanoparticles were characterized by Fourier transform infrared (FTIR) spectroscopy, UV–visible spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), electron-dispersive (EDX) spectrum and water contact angle (WCA) measurements. The application of Cu and Al nanoparticles was tested towards the catalytic reduction of 4-nitrophenol (NiP), hexavalent chromium {Cr(VI)} and rhodamine 6G (R6G) dye in the presence sodiumborohydride (NaBH₄) as a reducing agent. From the UV–visible spectrum, the reduction rate constant (k_{app}) and the induction time (T_i) were determined and compared critically. The HRTEM analysis confirmed the nanosize of Cu and Al prepared by a simple chemical etching process followed by the chemical reduction method.

Keywords Nanostructure · Characterization · Water contact angle · Catalyst · Reduction

Introduction

The environment is spoiled due to the various activities of human beings such as industrialization, modernization and civilization. Among these, the industrialization plays a vital role in disturbing the environmental quality because of the effluents that are highly toxic and hazardous, and simply disposed into the open environment, for example, the nitrophenols (NiP) from chemical industries [1, 2], hexavalent chromium [Cr(VI)] from chromium industry, metal finishing industry, tannery [3] and dye effluents from dye and textile industries [4, 5]. When they are disposed into

the open environment, they degrade the quality of soil and water highly. Hence, it is necessary to remove the pollutant or to reduce the pollution due to phenolic compounds, particularly NiP, dye effluents and Cr(VI) ion. On the other hand, the reduced product of NiP plays a vital role in the pharmaceutical field as a starting material for the preparation of drugs and it is not possible to remove the NiP from the chemical industry. Moreover, the catalytic reduction of NiP is an interesting one because of its pseudo-first-order kinetics. Hence, the reduction of NiP using various catalyst systems is the only way to reduce the pollution caused by the NiP. Currently, various catalyst systems such as iron niobate [6], hydroxyapatite [7], Au nanoparticles (NP) [8], Au–SiO₂ [9], layered double hydroxides (LDH) [10], TiO₂ [11], Al₂O₃ [12], Pd–Ag [13], AC–Ag [14], Au–CeO₂ [15], aminoclay–Fe NP [16], Clay–Pt [17], Fe₃O₄ [18], Ni–Se [19] and Ni–P [20] are used for the reduction of NiP. Through study of the literature, any report based on the Cu and Al nanoparticles as a catalyst for the reduction of NiP in the presence of NaBH₄ is not found. Moreover, the Cu and Al nanoparticles formed as by-products during the chemical etching of metal surface followed by a chemical reduction are converted into useful materials such as catalyst for the reduction reaction.

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Cr(III) is less toxic when compared with Cr(VI). Hence, it is better to reduce the Cr(VI) using different methodology. Photocatalytic reduction of Cr(VI) over TiO_2 particles was reported by Testa et al. [21]. In 2014, Sadik and co-workers [22] studied the catalytic reduction of Cr(VI) using Pd NP. Cu(II)-catalyzed reduction of Cr(VI) was reported in the literature [23]. Goethite surface-assisted catalytic reduction of Cr(VI) was reported by Kim and research team [24]. In 2015, microbial system-catalyzed reduction of Cr(VI) was reported in the literature [25]. The literature survey indicates that the catalytic reduction of Cr(VI) by Cu and Al nanostructured catalyst system is not available so far. This urged the researchers to do the present investigation.

Rhodamine 6G (R6G) is a photostable organic fluorescent dye and has a wide range of applications in textile industry. Unfortunately, the conventional biological methods are less effective towards the degradation or color removal of R6G dye. In order to remove the color and to reduce the toxicity of R6G, it is necessary to reduce the structure of R6G in the presence of a catalyst. The catalytic reduction of R6G in the presence of Ag– SiO_2 nanocatalyst was carried out [26]. Other catalysts such as $\text{SiO}_2 @ \text{TiO}_2$ [27], ammonium phosphomolybdate [28], Au–Pd nanoalloy [29], TiO_2 [30], and Au– SiO_2 [31] were employed. Recently, Huang et al. used bismuth oxyiodide [32, 33] and bismuth oxycarbonate [34] for the photocatalytic degradation of various organic dyes. Few reports are available on the catalytic reduction of R6G in the presence of a nanostructured catalyst in the literature. During the fabrication of superhydrophobic (S.H) metal surfaces by a simple chemical etching process, hierarchically structured metal nanoparticles are formed as by-products. Very few applications are found for such hierarchic structured materials. The present investigation is made to extend the application of the S.H hierarchically structured metal after the chemical reduction method in the catalysis field. Catalysis is a developing field and considerable amount of research work is going on. The novelties of the present investigation are easy preparation, economically cheaper and no use of hazardous solvents.

Experimental

4-Nitrophenol (NiP, S.D. Fine Chemicals, India), potassium dichromate (PDC, S.D. Fine Chemicals), rhodamine6G (R6G, CDH Chemicals, India), myristic acid (MA, CDH Chemicals, India, etching agent) and sodium borohydride (NaBH_4 , Himedia chemicals, India, reducing agent) were purchased and used as received. Cu and Al metal plates (resource material) with 99% purity were purchased locally with the following dimensions: length 6 cm, breadth 2 cm, area 12 cm^2 . Double-distilled (DD) water was used for laboratory work.

The main aim of the present investigation is fabrication of low-cost S.H Cu and Al nanoparticles and extending their application towards the catalysis field. For the synthesis of S.H Cu or Al metal plates, a standard literature procedure was followed [35]. The Cu or Al plate with the area of 12 cm^2 was taken as a source material. The metal plate was cleaned with acetone and ultrasonicated for 1 h in an aqueous medium. Then the plate was removed from the ultrasonic bath and dried at 110°C for 2 h and it was weighed ($W_1\text{g}$) and subjected to the chemical etching reaction in the presence of 0.10 g MA in 100 mL ethanol medium under mild stirring condition. After 7 days of chemical etching, the metal plate was removed from the reaction medium and dried at 80°C for 2 h ($W_2\text{g}$). The content of the medium was dried at 80°C for a night. The metal with hierarchical structure was obtained as a powder, weighed ($W_3\text{g}$) and stored in a zip lock cover. During the fabrication of S.H Cu or Al plate, the etching agent-coated Cu or Al is formed as a by-product without any use. Thus, obtained hierarchically structured Cu or Al powder was dispersed in an aqueous medium with the aid of ultrasonication for 30 min. Once the dispersion was completed, excess of NaBH_4 was added under ultrasonication. The hierarchically structured Cu or Al is now subjected to chemical reduction reaction and reduced to Cu and Al nanoparticles. The reduction reaction was allowed to continue for another 30 min. At the end of the reaction, the dark-colored precipitate was filtered, dried, weighed and stored in a zip lock cover under nitrogen atmosphere.

Catalytic reduction study was carried out by the standard procedure [7]. 2 mL of $6.3 \times 10^{-5} \text{ M}$ NiP or $1.1 \times 10^{-5} \text{ M}$ $\text{K}_2\text{Cr}_2\text{O}_7$ or $2.17 \times 10^{-5} \text{ M}$ R6G solution was taken in a 3-mL capacity quartz cuvette microreactor. $1 \times 10^{-3} \text{ g}$ of Cu or Al nanoparticle catalyst was weighed and added to the micro-reactor. 15 mg of NaBH_4 was added in excess to the nanoreactor. While adding NaBH_4 in the presence of a nanocatalyst, the NiP was converted into aminophenol and is mentioned in Scheme 1. The reduction reaction was

Scheme 1 Reduction of 4-NP, Cr(VI) and R6G

quantitatively measured with the help of the UV–visible spectrophotometer at the interval of 1 min.

UV–visible spectrum (Shimadzu 3600 NIR, Japan) for samples was recorded in aqueous medium from 250 to 550 nm. Water contact angle (WCA) was measured by Kyowa DMS-200, Japan model instrument. The surface morphology with EDX spectrum was scanned by SEM, JSM 6300, JEOL model instrument. FTIR spectra for the samples were recorded with the help of Shimadzu 8400 S, Japan, instrument by KBr pelletization method from 400 to 4000 cm^{-1} . HRTEM image of the Cu and Al salts were recorded with the help of TEM 3010, JEOL instrument. The binding energy was determined by XPS (XPS, Thermo Scientific, Theta Probe, UK).

Results and discussion

Figure 1 indicates the FTIR spectra of MA-encapsulated metal nanoparticles. Figure 1a confirms the FTIR spectrum of MA-encapsulated Cu nanoparticle. The C–H symmetric and anti-symmetric stretching appeared at 2845 and 2910 cm^{-1} , respectively [35]. The C=O stretching of long-chain aliphatic carboxylic acid appeared at 1710 cm^{-1} . The C–O linkage appeared at 937 cm^{-1} . The metal–oxide (M–O) stretching appeared at 544 cm^{-1} . Figure 1b represents the FTIR spectrum of MA-encapsulated Al nanoparticle. Peaks appeared as explained earlier. Thus, the FTIR spectrum confirmed the MA-encapsulated Cu and Al nanoparticle formation.

The surface morphology of the MA-encapsulated Cu nanoparticle is given in Fig. 2a. The image indicates the presence of both rod and spherical particles. The length of

the rod shape was determined as 3–5 μm with the breadth of less than 700 nm. The arrow mark confirmed the same. The sphere-shaped NP with the size of 150 nm is also seen. Figure 2b indicates the SEM image of MA-encapsulated Al. The morphology of MA-encapsulated Al NP is entirely different from the MA-encapsulated Cu NP. The Al–MA system exhibits gel-like morphology with more number of micro-voids. One or two NP are also seen in the circled area. This type of material is very much useful in drug delivery and catalytic application. The size of the voids is varied from 2 to 5 μm . Hence, the SEM images confirmed the presence of nanostructured Cu–MA and Al–MA systems [36]. For the sake of comparison, the SEM image of pristine Cu and Al NP is given in Fig. 2c, d, respectively. Here also one can see the spherical and rod-shaped Cu NP. In the case of Al NP, some gel-like morphology is seen. This concludes that even after the chemical etching process with simultaneous encapsulation, the surface morphology of the Cu and Al NP is not changed.

Figure 3a indicates the HRTEM image of Cu–MA system. Here one can see the fiber and plate-like morphology. Agglomerated structure is also observed. The length of the fiber was found to be 1–4 μm with the breadth of ~150 nm. The length and breadth of the plate were calculated as 800 and 250 nm, respectively. Figure 3b represents the HRTEM image of Al–MA system with nanoparticle-like morphology. The size of the particle varied between 20 and 80 nm. Hence, the HRTEM images confirmed the nanostructure of Cu–MA and Al–MA systems.

In the present investigation, water-insoluble Cu–MA and Al–MA were prepared. To confirm the heterogeneity of the catalysts, water contact angle (WCA) was measured. Figure 4a represents the WCA image of Cu–MA and Fig. 4b represents WCA image of Al–MA systems. The WCA was determined as 147° and 140.1°, respectively, for Cu and Al systems. Among these two systems, the Cu–MA system exhibited the S.H character. The fluorinated long-chain aliphatic acid also exhibited similar WCA [36]. Hence, the WCA measurement confirmed the SH and heterogeneous catalytic nature of Cu–MA and Al–MA systems.

The percentage of elements present in the systems can be determined by the EDX spectrum. Figure 5a indicates the EDX spectrum of Cu–MA system and Fig. 5b represents the EDX spectrum of Al–MA system. From Fig. 5a, the content of Cu was determined as 1.84%. Figure 5b shows the content of Al as 2.68%.

The XPS gives an idea about the outer most energy level of a material. Figure 6a represents the XPS of Cu–MA system. The appearance of $\text{Cu}2p_{1/2}$ (953.1 eV) and $\text{Cu}2p_{3/2}$ (932.2 eV) confirmed that Cu is in nanosize. This is in accordance with the literature report [33]. The XPS of nano-sized Al–MA is given in Fig. 6b. The $\text{Al}2p$ is appeared at

Fig. 1 FTIR spectrum of (a) Cu salt, (b) Al salt system

Fig. 2 SEM image of **a** Cu-MA, **b** Al-MA system, **c** Cu, **d** Al system

Fig. 3 TEM image of **a** Cu-MA, **b** Al-MA system

Fig. 4 WCA image of **a** Cu-MA, **b** Al-MA systems

Fig. 5 EDX spectrum of **a** Cu-MA, **b** Al-MA systems

Fig. 6 XPS of **a** Cu2p, **b** Al2p

72.6 eV [37]. Thus, the XPS confirmed the formation of nano-sized Cu-MA and Al-MA.

In the present investigation, the above-synthesized Cu and Al nanoparticles were tested towards the catalytic reduction of NiP, PDC and R6G. The catalytic activities of metal nanoparticles toward three different reactions were tested. Catalytic reduction of NiP involves the conversion of nitro group into amino group. Catalytic reduction of PDC involves the conversion of Cr(VI) into Cr(III). Similarly, the catalytic reduction of R6G involves the conversion of R6G into reduced form of R6G, i.e., the reduction of extended double bond. The catalytic reduction activity is identified with the help of UV–visible spectrophotometer.

Generally, metal or metal oxide NP is considered as an efficient catalyst system for the catalytic reduction reaction. The common example is the catalytic reduction of NiP at room temperature. The reduction follows a pseudo-first-order kinetics and it is considered as a model compound [38]. In the present investigation, an attempt is made towards the catalytic reduction of NiP using Cu and Al nanoparticles. The catalytic reduction was quantitatively followed with the help of UV–visible spectrophotometer. The UV–visible spectrum of NiP exhibits an absorbance peak at 401 nm (Fig. 7a). After the addition of the catalyst and NaBH₄, the absorbance reduced drastically at 401 nm within 6 min. This confirmed that the Cu-MA system is an efficient catalyst towards the reduction of NiP in Fig. 7b–g. The reduction of NiP into aminophenol proceeded through the formation of phenolate anion. To find out the reduction rate constant, the plot of time against $\ln(A/A_0)$ (Fig. 7h) was drawn. The plot showed a straight line with negative trend. From the slope value, the apparent rate constant (k_{app}) was calculated as $17.8 \times 10^{-3} \text{ s}^{-1}$ (Table 1). The intercept value showed the induction time as 0.22 s. To compare the catalytic activity of Al nanoparticle, similar type of reduction study was carried out (Fig. 8a–k). The k_{app} value was determined from Fig. 8l as $16.2 \times 10^{-3} \text{ s}^{-1}$ with an induction time of 0.46 s (Table 1). The catalytic reduction study confirmed that the Cu nanoparticle is more efficient than the Al nanoparticle towards the catalytic reduction of NiP in the presence of NaBH₄. Both

Fig. 7 UV–visible spectrum of NiP taken at 1-min time interval in the presence of Cu–MA system a–g, the plot of time vs. $\ln(A/A_0)$ h

Table 1 The k_{app} and T_i values of the catalysts

System	k_{app} (s^{-1})	T_i (s)
Cu–MA–PDC	9.32×10^{-3}	5.59
Cu–MA–R6G	21.2×10^{-3}	4.19
Cu–MA–NiP	17.8×10^{-3}	0.22
Al–MA–PDC	6.44×10^{-3}	2.32
Al–MA–R6G	11.7×10^{-3}	2.06
Al–MA–NiP	16.2×10^{-3}	0.46

the k_{app} and induction time confirmed the same. The nano-structured system yielded higher k_{app} when compared with the literature value [7]. This proved the high catalytic nature of the nano-structured systems. The bio-based nanospheres [39] consumed 40 min for the complete reduction of NiP, but the present investigation consumed 11 min only. In 2017, Majumdar et al. [40] reported the Pd nanoparticle-mediated catalytic reduction NiP and the k_{app} value was reported as

$3.83 \times 10^{-3} s^{-1}$. Hence, when compared with the literature, the present investigation yielded better results.

The catalytic reduction of Cr(VI) into Cr(III) was carried out in the presence of Cu and Al nanoparticles as an individual catalyst using $NaBH_4$ as a reducing agent. Figure 9a–m indicates the UV–visible spectrum of Cr(VI) measured at time interval of 1 min in the given experimental conditions. For Cu–MA system, it was found that while increasing the reduction time the concentration of Cr(VI) at 372 nm reduced slowly. It means the Cr(VI) is converted into Cr(III). To find out k_{app} , the plot of time vs $\ln(A/A_0)$ (Fig. 9n) was drawn. The plot showed a decreasing trend. The slope and intercept values were noted from which the k_{app} value was calculated as $9.32 \times 10^{-3} s^{-1}$. The T_i was determined as 5.59 s. When compared with the literature [24], the present investigation yielded better results due to the nanostructure of the catalyst.

A similar experimental procedure was followed for the catalytic reduction of Cr(VI) using Al nanoparticle as a catalyst. Figure 10a–j indicates the UV–visible spectrum of

Fig. 8 UV–visible spectrum of NiP taken at 1-min time interval in the presence of Al–MA system a–k, plot of time vs. $\ln(A/A_0)$ l

Cr(VI) at 372 nm. Here, also while increasing the reduction time, the absorbance reduced at 372 nm. Again, this confirmed the reduction of Cr(VI) into Cr(III). The k_{app} was calculated from the plot of time vs $\ln(A/A_0)$ (Fig. 10k) as $6.44 \times 10^{-3} \text{ s}^{-1}$. The T_i was noted as 2.32 s. The Cu nanoparticle yielded the highest k_{app} and T_i values. The highest k_{app} value explained that the Cu nanoparticle has high catalytic activity rather than the Al nanoparticle due to smaller in size of Cu nanoparticle (Table 1). Both the Cu and Al nanoparticles produced better results when compared with the goethite-like catalyst [24].

The pollution or the toxicity of a material can be lowered by reduction or oxidation reaction. In the present investigation, the reduction reaction is considered. R6G contains one quinone ring and one eneiminium chloride functional group. During the reduction reaction, the eneiminium chloride reduced. This can be quantitatively measured with the help of UV–visible spectrophotometer. An absorbance peak reduced drastically at 526 nm (Fig. 11a–e) for the Cu–MA system-catalyzed reduction of R6G. The spectrum was recorded at the time interval of 1 min. The k_{app} value was calculated from the plot of time

Fig. 9 UV–visible spectrum of Cr(VI) taken at 1-min time interval in the presence of Cu–MA system a–m, plot of time vs. $\ln(A/A_0)$ n

Fig. 10 UV–visible spectrum of Cr(VI) taken at 1-min time interval in the presence of Al–MA system a–j, plot of time vs. $\ln(A/A_0)$ k

Fig. 11 UV–visible spectrum of R6G taken at 1-min time interval in the presence of Cu–MA system a–e, plot of time vs. $\ln(A/A_0)$ f

Fig. 12 UV–visible spectrum of R6G taken at 1-min time interval in the presence of Al–MA system a–g, plot of time vs. $\ln(A/A_0)$ h

Fig. 13 Plot of number of cycles against k_{app} (s^{-1}), a Cu–MA–PDC, b Cu–MA–R6G, c Cu–MA–NiP, d Al–MA–PDC, e Al–MA–R6G, f Al–MA–NiP systems

against $\ln(A/A_0)$ (Fig. 11f) as $21.2 \times 10^{-2} s^{-1}$ and the T_i as 4.19 s (Table 1). The Ag–SiO₂ catalyst system consumed longer time to complete the reduction of R6G [26]. The present catalyst systems yield a good result within a short period of reduction time. A similar type of plot was made for the Al–MA system (Fig. 12a–g). From Fig. 12 g, the k_{app} value was determined as $11.7 \times 10^{-2} s^{-1}$ and the T_i was determined as 2.06 s. The Cu–MA system exhibited the highest k_{app} value and high T_i value for Cu–MA system.

To confirm the catalytic effect of Cu and Al salts toward the reduction of Cr(VI), R6G dye and NiP, the reduction study was carried out for six repeated times for each system and their k_{app} values were determined. It is very interesting to note that even after the sixth cycle the k_{app} value is not decreased, i.e., the catalyst is stable towards the experimental conditions. This can be explained as follows: during the reduction reaction, the Cu and Al NP are simultaneously reduced and maintained their shape and size in each repeating cycle. Hence, there is no change in the k_{app}

value of the reaction while repeating the experiments. This confirmed the catalytic efficiency of the Cu and Al salts toward the reduction of Cr(VI), R6G and NiP-like pollutants. Figure 13a–f indicates the plots for Cu and Al salt catalyst systems.

In an overall study, the Cu–MA system exhibited the highest k_{app} value due to the small size of Cu atom. The important point to be noted in the study is T_i value. The T_i value of the Cu–MA system or Al–MA system for different reduction reaction is different. For example, the Cu–MA system, towards the reduction of Cr(VI), NiP and R6G, the T_i value was determined as 5.59, 0.22 and 4.19 s, respectively. This proved that the T_i value depends on the nature of the reaction medium, size and charge of the material to be reduced and the catalyst.

Conclusions

From the study, the following niche points are presented as conclusion. The FTIR spectrum confirmed the metal nanoparticle formation. The WCA measurement confirmed the SH nature of metal nanoparticles (147°). The SEM results declared the presence of nanometer-sized materials in the MA-encapsulated metal nanoparticles. The HRTEM image of Al nanoparticle declared the size as 20–80 nm. The EDX spectrum informed the higher percentage content of Al in the Al–MA system. The XPS showed the Al2p at 72.6 eV. The Cu–MA system exhibited high k_{app} ($2.12 \times 10^{-2} s^{-1}$) and high T_i (5.5 s) values for all the systems. The present investigation proved that a nanostructured material can effectively act as a catalyst for the reduction study.

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References

- Michalowicz, J., Duda, W.: Phenols and toxicology. *Polish J. Environ. Stud.* **16**(3), 347–362 (2007)
- Kumar, B., Tyagi, J., Verma, V.K., Sharma, C.S., Akolkar, A.B.: Distribution of eleven priority phenolic compounds in soils from mixed land use and assessment of health hazard from human pollution. *Adv. Appl. Sci. Res.* **5**(2), 125–132 (2014)
- Lonkar, N., Bozic, N., Andelkovic, I., Vujcic, Z.: Removal of aqueous phenol and phenolic derivatives by immobilized potato polyphenol oxidase. *J. Serb. Chem. Soc.* **76**, 513–522 (2011)
- Gad, N.S., Saad, A.S.: Effect of environmental pollution by phenol on some physiological parameters of *oreochromis niloticus*. *Glob. Veter.* **2**(6), 313–319 (2008)
- Mala, J., Cuikrova, M., Hrubcova, M., Machova, P.: Influence of vegetation on phenolic acid contents in soil. *J. For. Sci.* **59**(7), 288–294 (2013)
- Ghorai, T.K.: Synthesis of spherical mesoporous titania modified iron-niobate nano clusters for photocatalytic reduction of 4-nitrophenol. *J. Mater. Res. Technol.* **4**(2), 133–143 (2015)
- Sowmiya, S., Sowmiya, S., Kanchana, K., Jeyaselvi, J., Anita, M., Meenarathi, B., Anbarasan, R.: Synthesis, characterization and catalytic reduction activity of poly(epichlorohydrin-g-acid fuchsin)/hydroxyapatite nanocomposite. *J. Chem. Biol. Phys. Sci. Sec. A* **5**(4), 3801–3810 (2015)
- Majumdar, R., Bag, B.G., Maity, N.: *Acacia nilotica* leaf extract mediated size controlled rapid synthesis of gold nano particles and study of its catalytic activity. *Int. Nano Lett.* **3**, 53–58 (2013)
- Peng, Y., Leng, W., Dong, B., Gao, Y.: Bottom-up preparation of gold nanoparticle-mesoporous silica composite nanotubes as a catalyst for the reduction of 4-nitrophenol. *Chin. J. Catal.* **36**(7), 1117–1123 (2015)
- Ma, H., Wang, H., Wu, T., Na, C.: Highly active layered double hydroxide derived cobalt nano catalysts for *p*-nitrophenol reduction. *Appl. Catal. B Environ.* **180**, 471–479 (2016)
- Islam, S., Bormon, S.K., Hossain, K., Habib, A., Islam, A.: Photocatalytic degradation of *p*-nitrophenol in aqueous suspension of TiO_2 . *Am. J. Anal. Chem.* **5**, 483–489 (2014)
- Chen, R., Du, Y., Xing, W., Xu, N.: Effect of alumina particle on $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts for *p*-nitrophenol hydrogenation. *Chin. J. Chem. Eng.* **15**(6), 884–888 (2007)
- Javaid, R., Kawasaki, S.I., Suzuki, A., Suzuki, T.M.: Simple and rapid hydrogenation of *p*-nitrophenol with aqueous formic acid in catalytic flow reactor. *Beilstein J. Org. Chem.* **9**, 1156–1163 (2013)
- Ravula, S., Essner, J.B., La, W.A., Paroda, L.P., Kargupta, R., Hull, G.J., Sengupta, S., Batq, G.A.: Sun light assisted route to anti plasmonic amino clay. *Nanoscale* **7**, 86–91 (2015)
- Zhao, K., Qi, J., Zhao, S., Tang, Z.: Multiple Au cores in CeO_2 hollow spheres for the superior catalytic reduction of *p*-nitrophenol. *Chin. J. Catal.* **36**(3), 261–269 (2015)
- Vandarkuzhali, S.A., Radha, N., Pandian, K.: Water soluble amino clay for catalytic reduction of nitrophenol. *Orient. J. Chem.* **29**(2), 661–665 (2013)
- Varade, D., Haraguchi, K.: Synthesis of highly active and thermally stable nanostructured Pt/clay materials by clay mediated in situ reduction. *Langmuir* **29**(6), 1977–1984 (2013)
- Wu, J., Liu, Y., Bao, L.: A simple way to prepare Fe_3O_4 @polypyrrole hollow capsules and their application as catalyst supports in reduction of 4-nitrophenol. *Chem. Lett.* **44**(4), 557–559 (2015)
- Wang, X.W., Wu, K.L., Zhao, M.L., Yun, R.: $\text{Ni}_{0.8}\text{Se}$ nanostructures with plate like and particle morphology and their catalytic performance. *Chem. Lett.* **44**(4), 521–523 (2015)
- Qin, Z., Liu, Z., Wang, Y.: Promotion effect of Mo in amorphous Ni–P catalysts for the liquid-phase catalytic hydrogenation of nitrobenzene to aniline. *Chem. Eng. Commun.* **20**(3), 1338–1351 (2014)
- Testa, J.J., Grela, M.A., Litter, M.I.: Heterogeneous photocatalytic reduction of Cr(VI) over TiO_2 particles in the presence of oxalate. Involvement of Cr(V) species. *Environ. Sci. Technol.* **38**(5), 1589–1594 (2004)
- Sadik, O.A., Noah, N.M., Okello, V.A., Sun, Z.: Catalytic reduction of hexavalent chromium using Pd nanoparticles: an undergraduate nanotechnology laboratory. *J. Chem. Ed.* **91**(2), 269–273 (2014)
- Li, Y., Qin, C., Zhang, I., Zhou, L.: Cu(II) catalytic reduction of Cr(VI) by tartaric acid under the irradiation of simulated solar light. *Environ. Eng. Sci.* **31**(8), 447–452 (2014)
- Kim, C., Lan, Y., Deng, B.: Kinetic study of hexavalent Cr(VI) reduction by H_2S through goethite surface catalytic reduction. *Geochem. J.* **41**(6), 397–405 (2007)
- Xafenias, N., Zhang, Y., Banks, C.J.: Evaluating hexavalent chromium reduction and electricity production in microbial fuel cells with alkaline cathodes. *Int. J. Environ. Sci. Technol.* **12**(8), 2435–2446 (2015)
- Han, Q.Y., Li, G.A., Wang, D.X., Zheng, H.R.: Synthesis of Ag/ SiO_2 composite nano spheres and their catalytic activity. *Sci. Chin. Chem.* **57**(6), 881–887 (2014)
- Wilhelm, P., Stephan, D.: Photodegradation of rhodamine dyes using $\text{SiO}_2/\text{TiO}_2$ nanospheres. *J. Photochem. Photobiol. A Chem.* **185**(1), 19–25 (2007)
- Bansal, A., Sharma, D., Ameta, R., Sharma, S.: Photodegradation of rhodamine 6G in presence of semiconducting ammonium phosphomolybdate. *Int. J. Chem. Sci.* **8**(4), 2747–2755 (2010)
- Tang, M., Wen, G., Jiang, Z.: A label free DNAzyme cleaving fluorescence method for the determination of trace Pb^{2+} based on catalysis of Au/Pd nanoalloy on the reduction of rhodamine 6G. *Luminescence* **30**(3), 296–302 (2015)
- Aarthi, T., Madras, G.: Photocatalytic degradation of rhodamine dyes with nano TiO_2 . *Ind. Eng. Chem. Res.* **46**(1), 7–14 (2007)
- Wang, D., Li, G., Han, O., Zheng, H.: Synthesis of Au/ SiO_2 composite nanospheres and their catalytic activity. *J. Nanosci. Nanotechnol.* **16**(4), 3821–3826 (2016)
- Huang, Y., Xu, H., Yang, H., Lin, Y., Liu, H., Tong, Y.: Efficient charges separation using advanced BiOI based hollow spheres decorated with Palladium and Manganese dioxide nanoparticles. *ACS Sustain. Chem. Eng.* **6**, 2751–2757 (2018)
- Huang, Y., Li, H., Balogun, M.S., Wenyue Liu, W., Tong, Y., Lu, X., Ji, H.: Oxygen vacancy induced Bismuthoxyiodide with remarkably increased visible-light absorption and superior photocatalytic performance. *ACS Appl. Mater. Inter.* **6**, 22920–22927 (2014)
- Huang, Y., Li, K., Ying, L., Tong, Y., Liu, H.: Enhanced efficiency of electron–hole separation in $\text{Bi}_2\text{O}_2\text{CO}_3$ for photocatalysis via acid treatment. *Chem. Cat. Chem.* **10**, 1–7 (2018)
- Chen, H.H., Anbarasan, R., Kuo, L.S., Chen, P.H.: Fabrication of hierarchical structured superhydrophobic Cu surface by in situ method with micro nano scaled particles. *Mater. Lett.* **66**(1), 299–301 (2012)

36. Chen, H.H., Anbarasan, R., Kuo, L.S., Chen, P.H.: Synthesis, characterizations and hydrophobicity of micro/nano scaled heptadecafluoro nonanoic acid decorated copper nanoparticle. *Nano Lett.* **2**(2), 101–105 (2010)
37. Levis, W.K., Roserbenger, A.T., Gord, J.R., Crouse, C.A., Bunker, C.E.: Multispectroscopic (FTIR, XPS, and TOFMS-TPD) investigation of the core–shell bonding in sonochemically prepared Aluminum nanoparticles capped with oleic acid. *J. Phys. Chem. C* **114**(14), 6377–6380 (2010)
38. Salipira, K.L., Mamba, B.B., Krause, R.W., Malefetse, T.J., Durbach, S.H.: Carbon nanotubes and cyclodextrin polymers for removing organic pollutants from water. *Environ. Chem. Lett.* **5**(1), 13–17 (2007)
39. Huang, C., Hu, J., Fan, W., Wu, X., Qiu, X.: Porous cubic bismuth oxide nanospheres: a facile synthesis and their conversion to bismuth during the reduction of nitrobenzenes. *Chem. Eng. Sci.* **131**, 155–161 (2015)
40. Majumdar, R., Tantayanon, S., Braja, G.: Synthesis of Palladium nanoparticles with leaf extract of *Chrysophyllum cainito* (star apple) and their applications as efficient catalyst for C–C coupling and reduction reactions. *Int. Nano Lett.* **7**(4), 267–274 (2017)

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