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SHORT RESEARCH COMMUNICATION

Nanoparticle-assisted photo-Fenton reaction for photo-decomposition of humic acid

Jhuma Banik[1] · Srijita Basumallick[1]

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Abstract We report here the synthesis of CuO-doped ZnO composite nanomaterials (NMs) by chemical route and demonstrated for the first time that these NMs are efficient catalysts for H_2O_2-assisted photo-decomposition (photo-Fenton type catalyst) of humic acid, a natural pollutant of surface water by solar irradiation. This has been explained by faster electron transfer to OH radical at the p–n hetero-junction of this composite catalyst. Application of this composite catalyst in decomposing humus substances of local pond water by solar energy has been demonstrated.

Keywords Photo-Fenton reaction · Humic acid · CuO-doped ZnO composite nanomaterials

Introduction

Humic substances (HS) are natural organic matter (NOM), present in water bodies like ponds, lakes and rivers. HS are formed mainly by bio-degradation of plants by the process of humification. They are complex, heterogeneous poly-dispersed mixtures of organic substances whose compositions are not yet clearly known (Piccolo 2002). HS is generally present at ppm level in pond water and a slight excess makes the water brownish. During chlorination of water in drinking water plant, HS are converted to carcinogenic chloro-compounds (Breider and Albers 2015; Basumallick and Santra 2017); hence, they must be removed before water treatment.

Fenton (Fenton 1894) reagents are often used for decomposing organic pollutants from waste water. The reagent comprises of H_2O_2 and ferrous iron, and it generates hydroxyl radicals, which are reactive oxygen species (ROS) and oxidize organic pollutants including humic acid (Wang et al. 2012). The ferrous iron (Fe^{2+}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of OH radicals involves a series of reactions in an aqueous solution. Thus, H_2O_2 acts as an initiator for the generation of OH radicals, but OH radicals so generated easily recombine to form H_2O_2 again (Ebrahiem et al. 2013). In general, Fenton's oxidation process is coupled with UV radiation to accelerate the decomposition of H_2O_2 to OH radicals and known as photo-Fenton process and the reagent (Ebrahiem et al. 2013) is designated as ($UV/H_2O_2/Fe^{2+}$).

Recently, semiconductor photo-catalysts such as titanium oxide and zinc oxide have been applied for photo-degradation of contaminants in waste water and air (Fujishima 1972; Amy et al. 1995; Hariharan 2006; Daneshvara et al. 2004). The photo-catalyst, ZnO has also been considered as a suitable alternative for TiO_2, the most used and typical photo-catalytic material, due to their similar band-gap energies. Again, ZnO nanomaterials (NMs) are cost-effective, easily synthesized and environment friendly.

H_2O_2-assisted photo-Fenton reaction for the degradation of humic acid onto ZnO surface has been reported (Oskoeia et al. 2016). ZnO illuminated by UV, can photo-degrade humic acid by itself, presence of H_2O_2 enhances the degradation process (Oskoeia et al. 2016). But these processes use UV as a source of photo-illumination. This is costly and an energy-consuming process. We intend to use solar radiation for degradation of humic acid. We studied a similar reaction using ZnO nanoparticles illuminated by solar radiation at noon for three hours at our institute open

✉ Srijita Basumallick
srijitabasumallick@gmail.com

[1] Department of Chemistry, National Institute of Technology, Agartala 799046, India

space (23.8315°N, 91.2868°E) utilizing UV from solar radiation at neutral pH. We have noted considerable enhancement of the degradation process of humic acid by combined effect of ZnO and H_2O_2. We have extended our research by doping ZnO NPs with CuO by hydrothermal method to enhance their photo-catalytic efficiency (Saravanana et al. 2013; Chang et al. 2013), and tested the application of this composite catalyst for decomposition of humus substances of a local pond water.

Materials and method

ZnO nanopreparation: ZnO NMs of average size (50 nm) have been prepared by simple literature protocol (Ghorbani et al. 2015) mixing dilutions (0.1 M) of each of the solutions $Zn(NO_3)_2$ and KOH under vigorous stirring and calcined the washed precipitate at 50 °C.

CuO nanopreparation on ZnO: the NMs so formed (10 mg) were dispersed in 30 ml of 0.01 M $CuSO_4$ solution taken in a 100 ml hydrothermal bomb, where a precipitate of $Cu(OH)_2$ is formed by adding dilute KOH solution drop wise, and heated under hydrothermal condition at 80 °C for 1 h. The mixture was cooled, centrifuged and washed repeatedly with DI water, and dried under vacuum.

Photo-degradation study

The composite NMs were re-dispersed for characterization and photo-chemical studies. Photo-degradation study was carried out in a laboratory model photo-reactor, which is a simple glass vessel (250 ml) with a glass lead and an orifice for release of any gaseous product. An aqueous solution (150 ml) of sodium salt of humic acid (Loba Chemicals) at ppm concentration, mixed with 50 mg of ZnO/ZnO–CuO catalysts was taken within the reactors and exposed to direct sunlight at noon for 3 h. A similar setup was kept in dark. After each set of experiment the catalyst was recovered by leaching out the HA salt and reused for the next set. ZnO–CuO composite has been used as UV sensor (Park et al. 2015) and reported as a photo-stable material.

After 3 h humic acid concentrations were monitored spectrophotometrically at an absorbance of 254 nm.

Results and discussions

Figure 1 shows the UV–visible absorption spectra of very dilute dispersions of ZnO and ZnO-composite NMs. A characteristic ZnO absorption peak at 367 nm (black line) is observed with ZnO NMs, while the composite shows an additional peak at 266 nm (red line) indicating the presence of CuO.

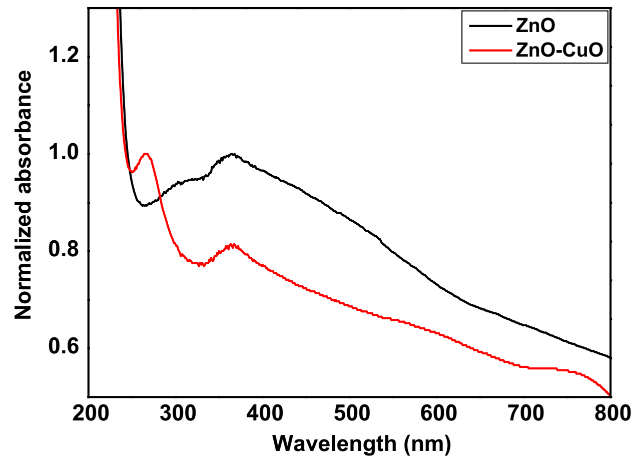


Fig. 1 UV–visible spectra of aqueous dispersions of ZnO (*black line*) and ZnO–CuO NMs (*red line*)

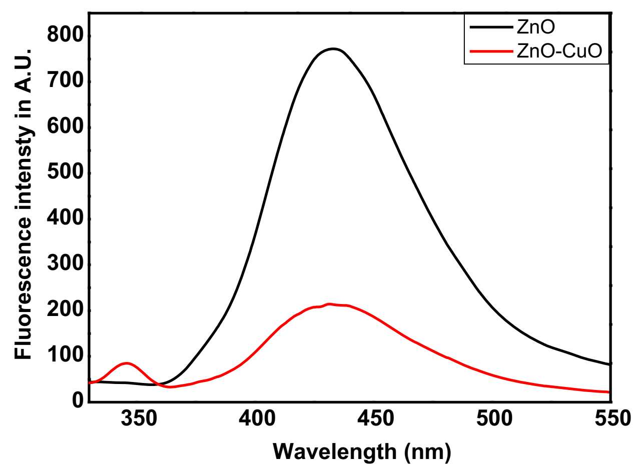


Fig. 2 Fluorescence spectra of aqueous dispersions of ZnO (*black line*) and ZnO–CuO NMs (*red line*)

The fluorescence spectra of prepared ZnO NMs are shown in Fig. 2 (black line), a similar spectrum for the composite NMs is shown in red line. Observed quenching of ZnO fluorescence clearly indicates formation of composite NMs. XRD of the composite NM is shown in Fig. 3, which is similar to that of reported XRD data of ZnO, but appearance of peaks at 38.8° indicates the incorporation of CuO (Jai et al. 2012) within crystal structure of ZnO. Close scrutiny of XRD image indicates slight shift of peak position of ZnO relative to JCPDS 8000-75 data, for instance the peak at 31.728(100) and 34.400(002) for pure ZnO are shifted to 31.6601 and 34.4201, respectively . Similarly, peak at 38.736 for CuO (JCPDS 8019-17) is shifted to 38.8001. This may be due to the formation of

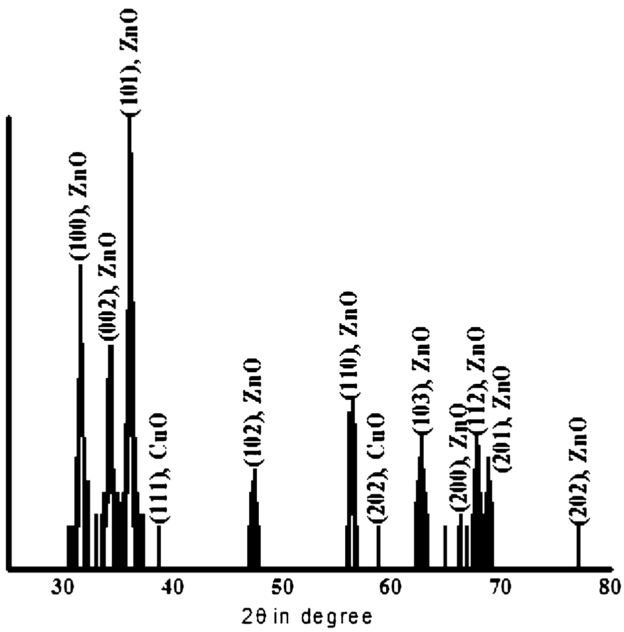


Fig. 3 XRD of ZnO–CuO nanocomposites

alloy-type composites of ZnO–CuO as expected from the almost similar ionic radii of Zn^{2+} and Cu^{2+}. Since peak intensities of CuO are small and associated with noise peaks, it is likely that wurtzite structure of ZnO with unit cell parameters $a = b = 3.25$A and $c = 5.21$A is almost retained in ZnO–CuO composite.

SEM image of the composite ZnO–CuO particle is shown in Fig. 4. It is seen that the particles are mostly rod shaped, approximately 50–200 nm in size, and mostly agglomerated.

Percentages of humic acid photo-chemically degraded (subtracting values for the dark reactions) are shown in the bar-diagram (Fig. 5). Figure 5 is self-explanatory, and

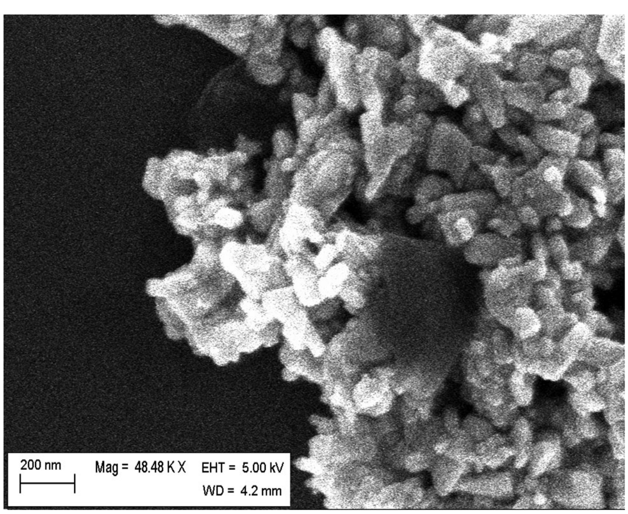


Fig. 4 SEM image of ZnO–CuO composite particles

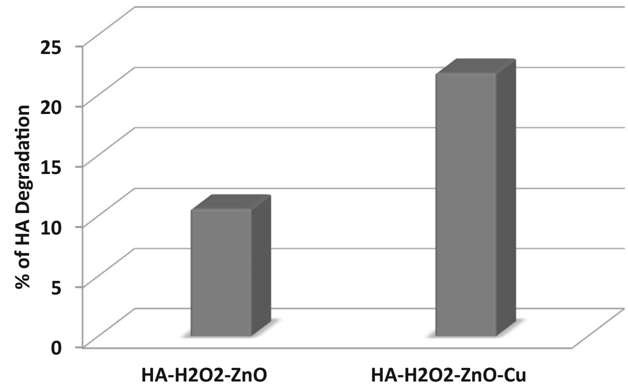


Fig. 5 Percentage of HA degraded by photo-Fenton type reactions under solar irradiation for 3 h

suggests that ZnO–CuO in the presence of H_2O_2 enhances photo-decomposition of humic acid under solar irradiation.

Photo-degradation study of water sample collected from a local pond

For this study, water samples from a local pond near our institute were collected in standard joint glass containers following literature protocol for such collections. The sample was filtered to remove any particles and allowed to stand for 12 h before the decanted sample was used for photo-decomposition study. The UV–visible spectra of the sample are shown (black line) in Fig. 6. The concentration of the HS present in the sample was measured by UV–visible spectra at −254 nm. The photo-decomposition study was carried out by the procedure stated above and UV–visible spectrum of the photo-catalytic decomposed solution is shown in Fig. 5 (red line).

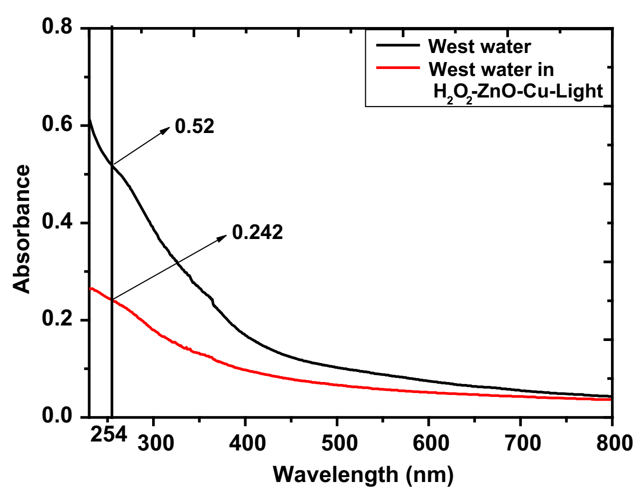
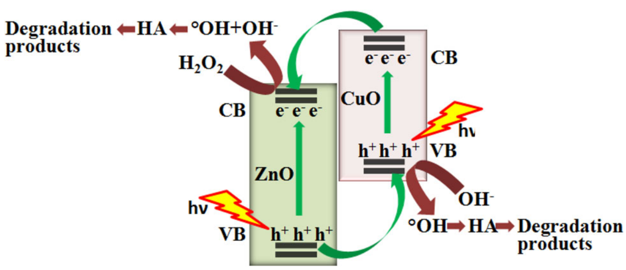


Fig. 6 Percentage of HA degraded by photo-Fenton type reactions under solar irradiation for 3 h in pond water

Proposed mechanism

It is known (Guo et al. 2013) that ZnO NMs can produce ROS under UV illumination as the potential of photo-excited hole at the valence band (2.6 V versus NHE at pH 7 and CB ~ -0.5 V versus NHE) (Oda et al. 2014; Dai et al. 2015) is much above the H_2O decomposition potential (1.48 versus NHE). H_2O_2 photodecomposed to OH radicals, and this OH radical can easily accept electrons at the conduction band of ZnO forming OH^- anion, similar to that of photo-Fenton reduction of OH by Fe^{2+} ion (Ebrahiem et al. 2013). Since CuO is a p-type semiconductor, it seems that electron transfer from CB of ZnO to OH at this hetero-junction (Yu et al. 2015) becomes faster, reducing radical (OH) recombination reaction. The mechanism of HA degradation, as explained above, is pictorially shown below:



Once OH radicals are easily formed on the semiconductor surface they oxidize (Goldstone et al. 2002) the humic acids to different low-molecular weight organic acids like acetic, formic, malonic, and oxalic acid.

Conclusions

From this preliminary study, we have demonstrated that ZnO–CuO composite NMs enhance Fenton-type photo-decomposition of humic acid, a natural pollutant present in surface water, by H_2O_2 under solar irradiation and suggested that electron transfer from CB of ZnO in the ZnO–CuO nanocomposite becomes faster to OH radical because of the presence of p–n hetero-junction at the composite NMs. When this composite catalyst is applied to study photo-decomposition of humus substances in local pond water, we observed a relative decomposition of humus substances to the extent of 53.5% in 3 h under mid-solar radiation (12.0–3.0 pm). From this preliminary study, we have demonstrated that ZnO–CuO composite nanomaterials enhance Fenton-type photo-decomposition of humic acid by H_2O_2 under solar irradiation and have a good application potential.

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