A facile surfactant assisted hydrothermal synthesis of ZnO and graphene loaded ZnO for efficient photocatalytic self-cleaning

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Abstract
Superhydrophilicity and photocatalysis are of great importance for self-cleaning applications. We report the synthesis of ZnO and ZnO loaded graphene nanostructures at different pH values with exposed polar facets by a simple hydrothermal method. Cetyltrimethylammonium bromide is used as surfactant and the synthesis is carried out without the aid of high temperature and demonstrated to have a superior photocatalytic activity. We observed a reduction in band gap for graphene loaded ZnO samples. Further, a one-step spin coating method is used for the preparation of optically transparent and photoinduced superhydrophilic ZnO hybrid films. We investigated the effect of cetyltrimethylammonium bromide capping agent on crystal growth and morphology of as synthesised samples. An effective improvement in photocatalytic activity of the nanohybrid (~100%) compared to pure ZnO (85%) is observed within 150 min. This can be attributed to the synergetic interaction of the components of the hybrid. Also, the hybrid samples coated on the glass substrate exhibits good transparency and superhydrophilicity upon UV irradiation. An unexpected transmittance as high as 84%–97% throughout most of the visible light region of the spectrum of the hybrid samples along with good photocatalytic efficiency and photoinduced superhydrophilicity makes the samples more suitable for self-cleaning applications.

1. Introduction
In recent years development of superhydrophilic materials (water contact angle less than 5°) with high photocatalytic activity has stimulated wide interest in materials research area with potential industrial applications including self-cleaning [1], anti-fogging [2], anti-microbial [3], textiles [4] etc. Semiconductor materials conjure up significant attention in this area due to their unique properties. ZnO is an n-type semiconductor exhibiting large direct band gap, good photosensitivity and excellent chemical stability and has been widely investigated by various researchers [5]. The properties of ZnO which make it highly applicable for self-cleaning, can be tuned by carrying out different morphology controlled synthesis procedures. Many fabrication techniques such as sol-gel method [6], hydrothermal method [7], microwave [8], physical vapour deposition, chemical vapour deposition [9] etc has been adopted to modify the crystal facets and morphology of ZnO nanostructures. Among these, hydrothermal route is best known method to achieve morphology controlled growth. Adopting the use of Cetyltrimethylammonium bromide (CTAB) during hydrothermal treatment can electrostatically and stereochemically control the shape oriented growth of ZnO. CTAB as a structure directing surfactant ionises completely in solution to form CTA+ and Br−, and thereby fasten the crystallization of ZnO by dissolution and re-precipitation processes. Fageria et al reported CTAB assisted synthesis of flower like ZnO by solution precipitation method [10]. Wang et al synthesised ZnO nanopowders through hydrothermal method using CTAB as capping agent at a temperature 220 °C [11].

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Though the semiconductor oxide exhibits best photocatalytic activity, it possesses high electron-hole pair recombination which limits its application [12]. This problem can be solved by coupling ZnO with functional groups or doping with other metals [13]. Recently, carbon based materials such as carbon nanotubes [14], graphene [12] and reduced graphene oxide [15] has gained great attention due to their eccentric properties. Among these reduced graphene oxide is suitable material because it has high carrier mobility electron acceptor nature and large specific surface area which helps to achieve better photocatalytic activity by reducing electron-hole pair recombination. Lonkar and co-workers synthesised ZnO nanoparticles uniformly dispersed on the surface of thermally reduced graphene via solvent-less short-time ball milling of hydrozincite and graphite oxide [16]. Durmus et al developed graphene oxide nanosheets decorated with ZnO nanoparticle via two step sol-gel deposition method. The composite was used for photocatalytic degradation of basic Fuchsine dye and from the photonic stimulations of ZnO nanoparticles the mechanism is explained on the basis of electrochemical interactions between radical units and organic molecules [17].

The surfaces and interfaces, where redox reactions take place, have an important role in photocatalytic activity [18]. Consequently, most of the works focus on the ZnO nanostructures with exposed polar facets {1011} and {0001}, which are very difficult to get due to minimisation of surface energy during crystal growth. Liang et al successfully synthesised cone like ZnO mesocrystals enclosed by curved (10 11) and flat (000 1) surfaces through a facile precursor-hydrolysis process in a water/organic solvent system and explained the growth mechanism by Density Functional Theory [19]. Chen et al prepared anatase TiO₂ with dominant {001}, {101} and {010} facets by modified HF hydrothermal method and tested for photocatalytic oxidation of NH₃. They observed photocatalytic activity in the order of {001} > {101} > {010}, due to trapping of more photogenerated holes at the surface of high energy {001} facet [20]. Recently, Padmanabhan et al from our group synthesised anatase TiO₂ with variations in crystal morphology by modified hydrothermal method using CTAB as capping agent and investigated the photocatalytic activity towards methylene blue degradation [21]. Herein, we report the development of ZnO and graphene loaded ZnO nanostructures having good transparency by a facile low temperature hydrothermal method and its photocatalytic activity along with photoinduced superhydrophilicity were studied.

2. Experimental section

2.1. Materials
Zinc acetate dehydrate (99.0%) was purchased from Merck, India and cetyltrimethylammonium bromide (CTAB) from Spectrochem, India. Sodium hydroxide (NaOH, 97%) isopropyl alcohol (IPA, ≥99.0%), methylene blue (MB) powder, glacial acetic acid (reagent grade, 100%), sulphuric acid (H₂SO₄, 98%), potassium permanganate (KMnO₄, ≥98.5%) and hydrogen peroxide (H₂O₂, 30%) were obtained from Merck, India. Graphite powder with particle size <20 μm was purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2. Synthesis of nano zinc oxide
Nano ZnO was prepared by a modified hydrothermal method using CTAB as capping agent. Here, 0.06% of CTAB was dissolved in 100 ml of 1% glacial acetic acid solution. Zinc acetate dihydrate (0.001 M) was added to the above CTAB solution. Then the solution is stirred continuously for 24 h. The pH of the solution is adjusted to 12 with the addition of 1 M NaOH solution. The solution was then transferred into a 100 ml Teflon-lined stainless steel autoclave and it was kept at 100 °C for 7 h. The precipitate formed was washed and centrifuged with water several times and dried at 60 °C overnight. The obtained product was named as Z12. Synthesis is repeated with varying pH from 8 to 11 and samples were named as Z8, Z9, Z10 and Z11 respectively. A known amount of Z11 sample is calcinated at 500 °C for 4 h and is named as Z11-500 °C.

2.3. Synthesis of graphene oxide
Graphene Oxide (GO) was prepared from graphite using the modified Hummer’s method as reported previously [22]. Initially, graphite is dispersed in concentrated H₂SO₄ with continuous stirring for 12 h. KMnO₄ is added very slowly by maintaining the temperature of the reaction mixture below 20 °C, followed by 2.5 h stirring. Then water is added drop wise to the reaction mixture at room temperature and stirring was continued for 1 h. 30% H₂O₂ is then added to terminate the reaction. The so formed precipitate is washed and filtered with deionised water until neutral pH is obtained.

2.4. Synthesis of ZnO/reduced Graphene Oxide (rGO) hybrid
0.06% of CTAB was dissolved in 1% of glacial acetic acid solution. 0.001 M of zinc acetate dihydrate was added to the above solution followed by the addition of 3% W/W graphene oxide (with respect to ZnO formed)
Powder samples of ZnO and graphene-loaded ZnO were characterized by X-ray diffraction (XRD) and various measurements.

The crystallinity of the samples were measured by X-ray diffraction pattern, and the pattern of nano ZnO formed precipitate was washed, filtered by water repeatedly, which is followed by drying at 60 °C overnight. The obtained ZnO/rGO hybrid is named as Z11G3. Synthesis is repeated with varying weight percentage of GO, 5, 11 and 22 to obtain the samples Z11G5, Z11G11 and Z11G22 respectively.

2.5. Characterization and measurements

Powder samples of ZnO and graphene-loaded ZnO were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM) analysis. The crystal phases and size were evaluated by X-ray diffraction (XRD, PANalytical X’Pert Pro, \( \lambda = 1.5418 \) Å). The diffraction patterns were registered within the 2θ angle range from 10° to 80°. The morphology of the prepared samples was observed using a Carl Zeiss (UltraPlus) field emission scanning electron microscope (FESEM). Scanning and high resolution transmission electron micrographs were recorded with a JEOL JEM-2100 microscope. The transmittance of samples was measured by diffuse reflectance spectroscopy recorded using Agilent Cary 5000 UV–Vis spectrophotometer over the range of 200–800 nm and photoluminescence behaviour of the synthesized nanomaterials were studied by a spectro-fluorophotometer Jobin Yvon Horiba Model Fluorolog at an excitation wavelength of 320 nm. The photocatalytic activity was observed using a double beam UV-visible spectrophotometer (PerkinElmer UV/VIS Lambda 365).

The photocatalytic activities of the nano ZnO and the hybrid samples were evaluated by the degradation of methylene blue (MB) with a concentration of 10 ppm in an aqueous solution under UV light. Here, a self-designed photoreactor with a wavelength of 254 nm and intensity of 6.0 \( \times 10^3 \) W cm\(^{-2}\) (four Philips 30 W UV lamps) is used as the UV light source. The catalytic efficiency of dye degradation was calculated. In a typical process, 10 mg of photocatalyst was added to 40 ml of aqueous solution containing dye with a concentration of 10 ppm. Then, the solution was kept in the dark for 30 min to reach adsorption–desorption equilibrium of the dye on the ZnO surface before irradiation. A sample of about 5 ml was taken to determine its initial concentration prior to illumination. Next, the suspension was exposed to UV lamp to degrade the dye. 5 ml aliquots was taken out at a 30 min time interval and centrifuged to remove photocatalyst particles. The photocatalytic decomposition of MB was evaluated by recording the decrease in the absorbance of MB (\( \lambda_{\text{max}} = 663 \) nm) in the presence of the samples as a function of the irradiation time. The superhydrophilicity of the ZnO and hybrid samples were evaluated by water contact angle measurements at room temperature with a Rame hart Instrument co. 250 U1 from Succasunna, USA upon UV irradiation. For contact angle measurement, the dispersed sample (1 mg ml\(^{-1}\) of sample in isopropanol) was coated in 10 layers on a glass substrate by spin coating method and the measurement is taken for regular 30 min interval with UV irradiation.

3. Results and discussion

The crystallinity of the samples were measured by X-ray diffraction pattern, and the pattern of nano ZnO prepared by hydrothermal method at different pH values is provided in figure 1. The peaks located at 2θ = 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.9°, 66.3°, 67.9° and 69.1° are assigned to the diffraction planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) are observed for samples with pH of the reaction medium 10 or higher, corresponds to pure ZnO hexagonal wurtzite phase (ICPDS no. 36-1451).

Absence of any additional diffraction peaks confirms the synthesis of pure ZnO with high crystallinity. The samples synthesised below pH 10, Z8 and Z9 show a zinc hydroxide peak at 33.1° (marked peak) \([23]\) indicates...
that at lower pH, complete conversion of zinc hydroxide to ZnO does not occur. This may be due to the lower concentration of OH\(^-\) which influences the nucleation and growth of ZnO nuclei in the initial stage. Based on Scherrer formula, crystallite size is calculated from the XRD pattern. The FWHM values were decreased with increase of NaOH concentrations indicating the increase of the crystallite size. The crystallite size of the ZnO samples is found to be 20 nm, 24 nm and 28 nm for Z10, Z11 and Z12 respectively.

The morphology of the nano ZnO photocatalyst was examined by scanning electron microscopy analysis and pH of the growth solution play crucial roles in modifying the morphology of ZnO nanostructures. Figure 2 (a) reveals that, when pH of the growth solution is 11 using NaOH solution, a cone like nanostructure with rough surface is grown. At higher pH, concentration of OH is higher which leads to rapid growth of ZnO nuclei in the solution. Hence, at pH 12, aggregation of nanostructures is occurred (figure S2). An increase in degree of aggregation is observed when pH of the growth solution changes from 10 to 12.

We used the zinc acetate dihydrate (Zn(CH\(_3\)CO\(_2\))\(_2\) • 2H\(_2\)O) as the precursor for ZnO which first hydrolyse to form zinc hydroxide Zn(OH)\(_2\) hydrosol. When pH of the solution reaches to 10 with the addition of NaOH solution, the crystal growth units [Zn(OH)\(_4\)]\(^2-\) will form through the reaction between Zn\(^{2+}\) and OH\(^-\) in the presence of CTAB. The Zn(OH)\(_2\) undergo dehydration process under hydrothermal condition which leads to the formation of ZnO. The capping agent CTAB plays a crucial role in the formation of cone like morphology of ZnO [24]. The CTAB is an ionic surfactant which dissolves in water to form a cationic CTA\(^+\) tetrahedron with long hydrophobic tail. Due to the presence of CTAB surfactant, the surface tension of the solution is reduced which helps ZnO to grow with exposed high energy facets. The electrostatic and stereochemical effects of CTAB controls the shape oriented growth of ZnO nanostructures. The [Zn(OH)\(_4\)]\(^2-\) also has a tetrahedron geometry. The electrostatic interaction between the negatively charged [Zn(OH)\(_4\)]\(^2-\) and positively charged CTA\(^+\) leads to adsorption of large CTA\(^+\) on the surface of growing unit. This reduces the interface energy between the solution and growing unit and results in \{0001\} facet oriented growth. CTAB also helps in preventing the ZnO particles from agglomeration (see figure S8 in the supplementary information and the corresponding explanation). TEM analysis also confirms the cone like nanostructure of ZnO with exposed polar facet as shown in figure 2(b). These polar surfaces attracts more hydroxyl anion/atmospheric oxygen through the chemical or physical adsorption.
to facilitate the generation of more oxidative species like \( \text{H}_2\text{O}_2 \) and hydroxyl radicals which enhances the photocatalytic efficiency.

The optical properties of the samples were measured using diffuse reflectance UV–vis spectroscopy (figure 3). The absorbance of all three samples decreases with increase in wavelength. An absorption peak is observed for all samples around 356 nm. The absorption edges of the samples Z10 and Z11 is 420 nm while that of Z12 is 423 nm. The inset of figure 3 shows the estimation of optical band gap of ZnO using Tauc plot. The direct band gap of ZnO is calculated by extrapolation of the linear region of the curve and by calculating the slopes of reflectance spectra based on Kubelka-Munk (KM) function [25]. The band gap energy of all nano ZnO samples are found to be 3.23 eV which is slightly less than the bandgap of bulk ZnO (3.37 eV) [26]. This can be attributed to the formation of surface defect states due to overlapping of valence band and donor level.

As discussed, graphene incorporation effectively increases the properties of ZnO as photocatalyst. The pattern of pure graphite (SI figure S3) shows a peak at \( 2\theta = 26.6^\circ \) corresponds to (002) reflection (JCPDS card No. 41-1487), while the pattern of graphene oxide obtained from graphite by modified Hummer’s method

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**Figure 2.** (a) SEM image (b) TEM image of Z11 sample (c) TEM image of Z11 showing cone like nanostructure with oxygen termination.

**Figure 3.** (a) DRS spectra of Z10, Z11 and Z12. (b) Calculated bandgaps of samples using Kubelka-Munk function.
exhibit a (001) reflection at $2\theta = 10.2^\circ$ (SI figure S4). The XRD patterns of the ZnO-rGO hybrids synthesised at pH 11 by varying weight ratios of GO (figure 4) shows characteristic peaks of hexagonal wurtzite ZnO structure and all the diffraction peaks are sharp which indicate that the products formed are well crystallised. The absence of graphitic peak at 10° in the XRD pattern of hybrid indicates the exfoliation of graphene layers due to growth of ZnO. The broad peak at $2\theta = 26.35^\circ$, confirming the presence of graphene in the ZnO/rGO hybrids. The crystallite size of ZnO in hybrid is calculated and found to be slightly higher compared to pure ZnO prepared by hydrothermal method under the same condition. Among all hybrids, Z11G5 has the lowest crystallite size (37 nm) as shown in the table SI (S5).

The optical properties of the sample were measured by UV-visible and photoluminescence spectra. UV-visible spectra of the ZnO loaded graphene is shown in figure 5(a). Graphene oxide exhibits a wide absorption peak in the entire UV–visible region. Z11 shows a typical spectrum of ZnO with quite good absorption in the ultraviolet region having sharp absorption edge at 362 nm, while a notable broad and intense absorption in the visible-light region is observed for ZnO loaded graphene samples due to the introduction of graphene. Graphene oxide sheet form an energy level between the valence and conduction bands, results in narrowing the band gap. The band gap decreases with increase in the weight percentage of GO in the hybrid samples (figure 5(b)). The band gap is reduced to 3.03 eV (hybrid having 22% W/W of GO) from 3.23 eV (pure nano ZnO). This reduction in band gap can be attributed to the close interaction of ZnO and $\pi$ electron cloud of graphene sheets. These results indicate that the graphene loaded ZnO samples can act as an active photocatalyst.

Further, photoluminescence (PL) spectra of the samples synthesized at different weight ratios of GO were measured when the samples dispersed in H$_2$O with an excitation wavelength of 325 nm at room temperature is shown in figure 6. Pure ZnO have a strong UV emission at 379 nm and a weak visible emission at 467 nm. The UV region emission should be attributed to near band edge transition and the visible emission is caused by the transition in defect states. As shown in the figure 6 upon addition of GO, a blue shift is observed in emission maximum of the ZnO in the hybrid samples. It was found that a gradual decrease in intensity of both UV and visible peaks with the addition of graphene. This gradual decrease in fluorescence intensity of hybrids when compared to pure ZnO suggests an additional pathway for the disappearance of charge carriers due to interaction of graphene with the excited ZnO. TEM micrographs of graphene oxide and graphene loaded ZnO
are shown in figure 7. It is clear from the figures that spindle shaped ZnO is decorated on the surface of exfoliated reduced graphene oxide sheets. This further proves the exfoliation of graphene sheets in presence of ZnO.
Further specific surface area of Z11 and Z11G5 was estimated by N₂ adsorption/desorption analysis as shown in figure 8. The samples, Z11 and Z11G5 show type IV isotherm and a pore diameter of ∼5 nm. The specific surface area of Z11 (16.65 m² g⁻¹) higher than that of Z11G5 (4.06 m² g⁻¹). This reduction in specific surface area of Z11G5 hybrid sample is due to the intact interaction between the ZnO and graphene sheets which reduces the exposed free surface of the hybrid sample.

3.1. Photocatalytic study

Photocatalytic degradation of the sample Z11 was measured using methylene blue (MB) as an organic pollutant and monitored the decolourisation of dye in presence of catalyst under UV irradiation. Pure ZnO at pH 11 (Z11) shows photocatalytic efficiency of 83% within 180 min. Photocatalytic activity of ZnO synthesised at different pH was determined (Z10, Z12) and it seems Z10 and Z11 shows the highest photocatalytic activity (SI (Figure S6). The kinetics of the degradation reaction was fitted with pseudo-first order reaction and the apparent rate constant k (min⁻¹) was evaluated quantitatively. Figure 9 (a) shows the logarithmic plot of all nano ZnO samples. The rate constant of samples Z10, Z11 and Z12 being 0.010 46 m⁻¹, 0.009 42 m⁻¹ and 0.007 66 m⁻¹ respectively.

Figure 9(b) shows the logarithmic plot of ZnO/graphene hybrid samples and the sample Z11G5 shows highest photocatalytic efficiency of almost 100% within 180 min of UV irradiation while pure ZnO has only 83% degradation. However, for hybrids, the degradation efficiency first increases and then decreases with increase in the weight percentage of GO (SI (S7)). Upon calcination ZnO nanoparticles get agglomerated reducing the surface area of photocatalyst. The morphology of ZnO nanoparticles are greatly changed thereby the exposed percentage of high energy facet is reduced. This directly reflects on the photocatalytic efficiency of the photocatalyst and hence photocatalysis is reduced for Z11-500 °C compared to Z11. (refer figure S9 in the supplementary information).
3.2. Contact angle measurement

The transmittance and wettability of pure ZnO and ZnO/graphene hybrid films were evaluated by UV–vis spectroscopy and water contact angle measurement. Figure 10(c) shows the optical transmittance spectra of pure ZnO and ZnO/graphene hybrids. The film coated with pure ZnO, Z11 shows a transmittance of 76%–89% in a wavelength range from 500–800 nm. However, Z11 sample coated surface showed water contact angle of 70° which changes to almost 0° with 120 min of UV irradiation (figure 10(a)). Compared to Z11 the hybrid samples show better transparency than pure ZnO sample. The hybrid samples Z11G3 and Z11G5 shows transparency of 82%–93% and 84%–97% respectively. Transmittance decreases with decrease in wavelength, due to the absorption by the band gap excitation of ZnO. In samples, pure ZnO and ZnO/graphene hybrids even though the thickness was almost similar for the transmittance study, hybrid samples shows higher transmittance percentage due to promising transparent property of graphene.

Figures 10(a), (b) shows water contact angle of pure ZnO (Z11) and ZnO/rGO hybrid before and after 120 min of UV irradiation. Z11 shows a water contact angle of 72° which changes to superhydrophilic nature with angle almost 0° upon 120 min of UV irradiation. The water contact angle reduces to 43° for Z11-500 °C compared to Z11 sample. Also shows a photoinduced wettability of 0° under UV irradiation for 60 min. This fast reduction in water contact angle of calcined sample compared to Z11 may be due to the porous surface generated during the calcination of ZnO. During calcination CTAB which is previously capped on the surface of ZnO will be removed and it may generate pores on the surface of the ZnO (refer figure S10 is available online at stacks.iop.org/MRX/6/125014/mmedia in the supplementary information) The hybrid with 3% W/W of GO has higher water contact angle of 93° due to the presence of graphene in the sample which changes to 25° with better transparency of 84%–97% in the visible region.
4. Conclusion

Highly photocatalytically efficient nano ZnO and ZnO loaded graphene with superhydrophilic nature upon UV irradiation have been developed by a facile hydrothermal method in presence of CTAB as a surfactant. The hybrid films have demonstrated good transparency in a wide range of wavelength. When the reaction is carried out at different pH, it seems that pH 10 onwards complete crystallization of ZnO occurs. Photocatalytic degradation of methylene blue is tested using different ZnO and hybrid catalysts. Z11G5 shows better catalytic activity compared to pure ZnO. Further loading of graphene oxide in the hybrid decreases its catalytic activity due to the phase separation of ZnO and rGO. Thus an optimum concentration of rGO is required to effectively enhance the photocatalytic activity of ZnO. Also, the hybrid sample shows high transparency with good superhydrophilicity upon UV irradiation. We can envisage these surfaces for practical applications to wide range of applications such as self-cleaning and antifogging etc.

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