ZnO/graphene based composites for photocatalytic degradation of dyes from water: A Review

Shrinivas C. Motekar

Department of Chemistry, Sunderrao Solanke Mahavidyalaya, Majalgaon 431131, Beed, Maharashtra, India.

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Abstract - Graphene based nanocomposites are widely used for photocatalytic wastewater treatment. They have been remarkably utilized for the modification of semiconductor photocatalysts owing to its outstanding properties such as large surface area, great thermal stability and high electron conductivity. Then again, zinc oxide (ZnO) as a photocatalyst exhibits exceptional qualities such as good photocatalytic property, high oxidation ability, high photosensitivity, chemical stability, non-toxicity, biocompatibility, pyroelectric and piezoelectric properties. However, it possesses certain limitations i.e. photocorrosion, absorption in ultraviolet region, etc. as a result of alteration due to demand of visible light active photocatalysts. Hybrid of ZnO and graphene based nanomaterials is the best substitute for the photocatalytic degradation of dyes in wastewater. This review presents the recent progress and strategies employed for the photocatalytic degradation of dyes using ZnO/graphene based composites. Graphene supported ZnO nanomaterials are improved electron collectors that reveal strong obstruction for electron-hole pair recombination and increase the visible light adsorption to exhibit dynamic use of solar energy.

Key Words: Graphene, ZnO, nanocomposites, photocatalyst, wastewater treatment

1. INTRODUCTION

Rapidly growing industrialization and population has resulted in water pollution which has become challenging for scientific community. The United Nation World Water Development report shows that nearly 748 million people on the earth do not get pure drinking water and it is concluded that industrial demand for water will grow by 400% by 2050 [1]. In developing countries, every year, poor sanitation and contaminated drinking water causes the death of around 3.2 million children [2]. Wastewater can be treated using various conventional methods such as adsorption coagulation, precipitation, flocculation, Fenton process, aerobic natural treatment and membrane separation process. But, the high operational and chemical budgets, long process time, complex sludge generation, sophisticated techniques and difficulties in separation restrict the use of these conventional methods. Moreover, these methods do not exhibit very good efficiency in water remediation. For instance, membrane separation techniques reveal short lifetime of membrane and exhibit poor selectivity during adsorption process as well as transfer less pollutants from one phase to the other that renders poisonous secondary pollutants [3, 4]. Therefore, there are growing demands to develop well-organized methods for effective water remediation.

In one instance, a novel and effective approach of advanced oxidation processes has been developed for the degradation of organic and inorganic contaminants present in polluted water. This approach effectively exploits the prominent reactivity of $OH^·$ radicals during oxidation which produce a chain of reactions to degrade aqueous pollutants into harmless products [5, 6]. In other green chemical techniques, heterogeneous photocatalysis using semiconductors aims for the efficient utilization of sunlight or artificial indoor illumination for water remediation applications [7, 8]. Heterogeneous photocatalysis removes contaminants from wastewater by producing transient hydroxyl radicals ($OH^·$). It is to be noted that $OH^·$ radicals with 2.8 eV oxidation potential degrade organic contaminants and convert products either into less harmful organic compounds or their mineral constituents. Since 1972, several metal oxides such as zinc oxide (ZnO), titanium dioxide (TiO_2), iron (III) oxide (Fe_2O_3), vanadium oxide (V_2O_5), Zirconia (ZrO_2), tungsten trioxide (WO_3) and niobium pentoxide (Nb_2O_5) etc., have been used as good photocatalysts for photocatalytic water remediation [9, 10]. Out of these metal oxide photocatalysts, ZnO, an n-type semiconductor possessing band gap near 3.22 eV, is a unique semiconductor used for water treatment owing to its outstanding properties such as good photocatalytic property, high photosensitivity, strong oxidation ability, chemical stability, non-toxicity, biocompatibility, pyroelectric and piezoelectric properties due to its size and shape [11]. Commonly, fine ZnO nanoparticles have enlarged surface area and higher number of active surface sites that aid for the adsorptive removal of contaminants as they favour photogenerated charge carriers to react with contaminants. On the other hand, graphene is an allotrope of carbon possessing hexagonal atomic structure. It has two dimensional sp^2 hybridized carbons to give honeycomb like crystalline framework with good conductivity. Graphene is a good support for epitaxial growth of other hexagonal nanostructures such as ZnO, SnO_2 and TiO_2. Moreover, graphene based semiconductors remarkably enhance the photocatalytic degradation performance of the host material. Graphene oxide (GO) with hydroxyl and carboxyl moieties exhibit notable dispersion in solvents that renders numerous chances for the fabrication of GO-based hybrid nanocomposites [12]. Various methods have been used

to fabricate graphene, photocatalytic ZnO nanomaterials and ZnO nanomaterials decorated graphene based nanocomposite materials. Nevertheless, it is very difficult to synthesize such nanohybrids without agglomeration and with perfect order of the particle size to exhibit outstanding photocatalytic performance.

This review focuses on the recent progress and various strategies employed for water remediation using zinc oxide nanoparticles decorated graphene (ZnO@G) nanocomposite for the removal of different dyes such as azure B, crystal violet, methyl orange, methylene blue and rhodamine B.

2. ZnO AS A PHOTOCATALYST

Photocatalysis using semiconductors has been immensely attracting the researchers owing to its outstanding capacity and cheap procedures to solve environmental problems. Several semiconductors such as ZnO, In_2O_3, SnO_2, TiO_2, SiO_2, ZnS, WO_3, TiO_2 (anatase), Fe_2O_3, CdS, a-Fe_2O_3 etc., are emerged as efficient photocatalysts for water remediation [13]. Metal sulphide semiconductors suffer from photoanodic corrosion, whereas a-Fe_2O_3 suffers from photocathodic corrosion and are therefore unstable. The systematic study revealed that ZnO and TiO_2 semiconductors exhibit superior performance as compared to other metal oxides for the photocatalytic degradation of pollutants [14]. TiO_2 exhibits photocatalysis under the irradiation of UV light and it absorbs a very limited portion of 4-5% from solar spectrum. From UV- visible absorption spectra it is evident that ZnO nanomaterial absorbs greater light quanta and it behaves as semiconductor owing to its electronic structure and band gap characterized by filled conduction band and valence band [15]. When the research on ZnO started in 1930, the research was basically on bulk samples that included issues such as doping, growth, transport, band structure, excitation, deep centres, surface polarities and bulk polarities, large excitation and luminescence [16]. Generally, ZnO crystal structure occurs in the form of cubic, rocksalt or wurtzite arrangement. The cubic (zinc-blende) structure of ZnO is stable only after growth of cubic substrates, whereas rocksalt (NaCl) form of ZnO is very scarce owing to its creation under high pressure [17]. Amongst the three forms, wurtzite structure of ZnO is highly thermodynamically stable. ZnO has a wide band gap of 3.3 eV and it exhibits various applications in photocatalysts, lasers, pharmaceutical products etc. In photocatalysis, it generates reactive oxygen species on its surface under the irradiation of UV light. Moreover, it absorbs a large portion of UV spectrum and abundant light quanta, which facilitate it in photocatalytic degradation performance for water remediation.

The distinctive chemical performance and electrostatic force of polar surface generate wide range of nanostructures like nanorings, nanosprings, nanobows and nanohelices [18]. Generally, ZnO can be synthesized in one, two or three-dimensional forms of which one dimensional form includes needles, nanorods, ribbons, springs, helixes, rings, combs and

wires; two dimensional structural arrangement includes, nanopellets and nanosheets and lastly, three dimensional structures occurs mostly in flower, dandelion, snowflakes etc. forms [19]. Albeit, ZnO is flexible, it has certain shortcomings like barrier in visible light absorption (absorbs only 43% of solar energy spectrum), absorption near-UV spectral region, wide band gap of 3.3 eV, aggregation of particles during photocatalysis and noticeable photocorrosion that remarkably obstructs the photocatalytic performance of ZnO [20]. ZnO photocatalyst shows remarkable recombination of charge carriers. The visible spectrum range and photocatalytic efficiency of ZnO can be further enhanced using different methods such as depositing noble metals like Ag [21], Pt [22], Pd [23], Au [24], doping rare earth metal ions like Ln^{3+} [25], Nd^{3+} [26], coupling ZnO with other metal oxides for example, ZnO-SnO_2 [27], ZnO-TiO_2 [28]. Nonetheless, the heterojunction of metal oxides show adverse health results owing to enhanced cytotoxic potential and toxicity of prepared nanomaterials. Accordingly, nanocomposites of heterojunction forms with carbon based nanomaterials such as graphene, GO, fullerenes carbon nanotubes, etc. perform efficiently to favour for photo-electrochemical reactions and energy change [29]. Nanocomposites exhibit improved photocatalytic performance by enhancing their structural and electronic possession as compared to pure photocatalysts [30]. Thus it is recommended to use heterojunction nanocomposite of ZnO and graphene based materials. It is to be noted that delocalized π-electrons of carbonaceous nanomaterials participate in the electron transfer process since they suppress recombination of charge carriers by trapping photogenerated electrons and acting as sink [31].

3. GRAPHENE AS A SUPPORT TO PHOTOCATALYST

Generally, carbonaceous materials are available in three forms viz. amorphous carbon, graphite and diamond. These forms depend on the particular arrangement of carbon atoms and thereby changed properties. Out of these three forms, graphene is very recent addition. Considering carbon nanotubes and other carbonaceous materials, graphene with two dimensional nanosheets has received tremendous attention owing to its extensive potential relevance, involving energy transformation and storage [32]. Graphene is available in two other forms viz. GO and rGO (reduced Graphene Oxide), of which rGO can be synthesized by reducing GO. It is to be noted that rGO shows excellent performance in photocatalytic reactions. Several of these carbonaceous nanomaterials are used with heterojunction fabrication for various applications. Nanomaterials exhibit high surface area, shape dependent electronic, optical and catalytic properties and therefore, they can be used to synthesize potential catalysts for water remediation [33]. Carbonaceous materials reveal large surface area, high number of active sites, great porosity and therefore, they too can be proficiently used for the adsorptive removal of pollutants without releasing toxic

substances to purified water [34]. The first synthesis report on GO was given in 1859 by Oxford chemist, Benjamin C. Brodie, then in 1898 by Staudenmeier and in 1958 by Hummers et al. by reaction of graphite with fuming nitric acid and potassium chlorate [35-37]. GO is a thin, monomolecular form of carbonaceous nanomaterial created from graphite oxide by an alternative route to graphene. Albeit, GO act as an insulator, its electronic and mechanical properties can be altered by oxidation. The polar functional groups like carboxyl, hydroxyl and epoxy that are accountable for different surface-modified reactions at slightly alkaline pH, stabilize and thus facilitate the dispersion in water media on the GO surface [38]. For several years graphene was known, only theoretically, and was considered as thermodynamically unstable. Its first synthesis was accidental and in little quantity. It was first time observed in 1962 using electron microscope and was studied using supported metal surfaces. After many years, in 2004, Geim et al studied and reported the first publication on graphene showing isolation of single-layer from graphite[39]. In 2010, they were awarded Nobel Prize for this contribution. Graphene was studied owing to its outstanding electronic, chemical, physicochemical, mechanical, optical, thermal properties, large surface area and mobile electrons, which made graphene as a potential material for wide range of applications in biosensor, super capacitor, nanoelectronic, fuel cell, metal-free catalysis and drug delivery [40, 41]. Graphene was two dimensional material that was pragmatic in character. It had extensive honeycomb like network that could be rolled to one dimensional nanotube, stacked to form three dimensional graphite and enfolded to construct zero dimensional fullerenes. Graphene in the pure form is comprised of single layer of sp^2 carbon atoms bonded to render aromatic property. Graphene sheets are layered to show the lamellar graphite arrangement and the layers are separated by the distance of 3.34 Å [42]. Graphene has received tremendous attention for several theoretical studies and recently it is very interesting topic in research owing to the wide range of π-conjugation. Graphene exhibits potential combination with several metals such as Au, Ag, Pd, Pt, etc., metal oxides like ZnO, MnO_2, TiO_2, Fe_2O_3, Co_2O_4 etc., and polymers to develop hierarchical catalytic compounds [43]. It was considered that graphene support created from GO shows indispensable binding sites because of oxygen groups and defects present in GO in many instances. Preparation of rGO unified the control of oxygen amount and resolute the time and degree of oxidation and reduction situation [44]. Therefore, graphene based nanocomposites are regarded as an emerging research area for water remediation.

4. MECHANISM OF PHOTOCATALYTIC ACTIVITY OVER ZnO-GRAPHENE NANOCOMPOSITE

ZnO and graphene based nanocomposites were studied for the degradation of organic pollutants and it was found that graphene and its derivatives play a major role in the

augmentation of photocatalytic activity [45]. After the sunlight falls on the surface of ZnO-graphene nanocomposite, electrons get excited from valence band (vb) to conduction band (cb) (e_{cb}^-) and leave the holes (h_{vb}^+) behind. E_{cb} and E_{vb} of ZnO are -0.50 and +2.80V v/s NHE, respectively and that is suitable potential to create O_2^- and $OH^·$ radicals from O_2 and H_2O for the degradation of contaminants into non-toxic products i.e. CO_2 and H_2O. Graphene in ZnO serve in trapping excited e_{cb}^- in ZnO and thus stops the recombination with h_{vb}^+ .Consequently, it effectively plays the role of charge carrier sink and facilitates the transfer of excited e_{cb}^- under sunlight. The probable mechanism for the photocatalytic degradation of pollutants using ZnO-graphene nanocomposite is shown in the **Fig. 1**.
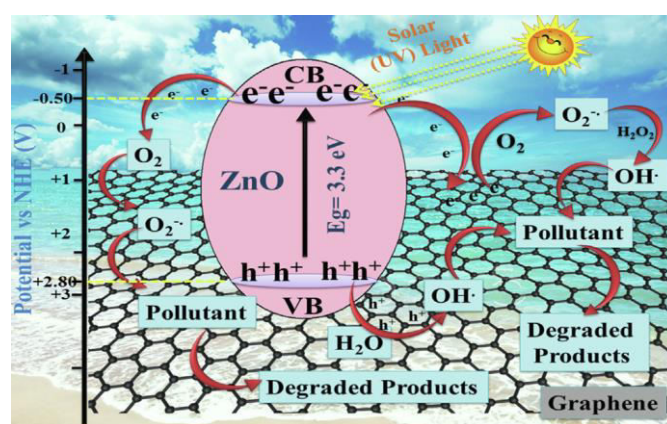
Fig -1: Proposed photocatalytic mechanism of ZnO/graphene based nanocomposite for pollutant eradication. Copyright 2019 The Authors. Production and hosting by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. [46].

Photogenerated electrons get reacted with the oxygen (O_2) to produce super oxide anion radicals (O_2^-). The huge separation rate of h^+ (holes) facilitates reaction with water molecules to produce hydroxyl radicals ($OH^·$) and electrons to produce super oxide anion radicals (O_2^-) after reaction with O_2. The radicals produced here degrade the contaminants onto the ZnO-graphene nanocomposite surface. The efficient electron transfer process on graphene sheets, which receives and transports the electrons, favours the photocatalytic degradation performance of the ZnO-graphene nanocomposite under sunlight. It is to be noted that graphene avoids recombination of charge carriers on the ZnO particle surface and enhances its photocatalytic degradation performance and thereby exhibits synergistic effect to improve the photocatalytic degradation capability of the ZnO-graphene nanocomposite [47, 48].

5. ZnO-GRAPHENE NANOCOMPOSITE PHOTOCATALYSTS FOR DYE DEGRADATION

In one instance, hierarchical ZnO-rGO nanocomposites were synthesized by hydrothermal method for the photocatalytic degradation of azure B dye [49]. The photocatalytic degradation of the azure B dye showed a

synergistic effect between photocatalytic ability of ZnO-rGO nanocomposites and surface adsorption characteristics. It was clearly found that the photocatalytic degradation capacity of ZnO was noticeably improved after hybridization with rGO. The results showed that ZnO-rGO nanocomposites remarkably adsorbed and photodegraded 99% of azure B dye under the irradiation of UV light within 20 min. rGO proficiently increased separation of electron-hole pair and extended the lifetime of charge carriers, which favoured for the advancement of interfacial charge transfer for adsorption and improved photocatalytic degradation of the azure B dye.

In one example, ZnO-GO nanocomposites were synthesized by chemical route for the photocatalytic degradation of crystal violet dye [50]. Herein GO was added during ZnO preparation to form ZnO-GO nanocomposite. The synthesized ZnO-GO nanocomposites exhibited fine optical properties and had improved interaction between ZnO and GO. Addition of GO remarkably enhanced size of ZnO nanoparticles in ZnO-GO nanocomposite. Moreover, accumulated ZnO nanoparticles were finely dispersed on GO sheets and more free surfaces on ZnO nanoparticles, formed after the addition of GO, enhanced surface interaction for quick photodegradation of crystal violet dye. ZnO-GO nanocomposites exhibited substantial photodegradation of crystal violet dye with maximum capacity of 95% under the irradiation of UV light within 80 min.

In one instance, ZnO-graphene nanocomposite was fabricated by wet chemical method that proficiently photodegraded methyl orange dye [51]. Herein, GO/ZnO nanocomposite and GO exhibited BET surface areas of 158.0 m^2 g^{-1} and 186.5 m^2 g^{-1}, respectively. It can be noted that nanocomposite shows lower surface area than GO because ZnO cubic voids reveal high density and low surface area. In one more example, ZnO-graphene nanocomposites were synthesized via a simple chemical corrosion process and it was employed for the photodegradation of methyl orange [52]. It was concluded from the results that the ZnO-graphene nanocomposites formed here possess a porous web like structure and that was favourable for the adsorption as well as mass transfer of dye and oxygen. The photodegradation efficiency of the 8 mg ZnO-graphene nanocomposite was 87% when irradiated under visible light for 180 min. The outstanding photocatalytic degradation capacity was owing to the porous web structure, electronic properties of the synthesized nanocomposites and lower band energy. Here graphene plays a vital role as it promotes the charge carrier separation and further suppresses charge carrier recombination and results into the enhancement of the photocatalytic degradation capacity.

In one example, ZnO microspheres-rGO nanocomposites were synthesized via simple solution method and the formation of these nanocomposites was confirmed from TEM images [53]. ZnO microspheres-rGO nanocomposites were used to degrade methylene blue under UV-irradiation. The BET surface areas for ZnO, ZRGO80, and ZRGO120 were 16 m^2 g^{-1}, 20 m^2 g^{-1} and 26 m^2 g^{-1}, respectively. It can be noted here that addition of rGO enhanced surface area of ZnO. In another instance, when ZnO-graphene nanocomposite was fabricated using methods involving multistep solution, it resulted into poor performance and liquid waste production in heavy quantities [54]. This method involves synthesis of ZnO graphene nanocomposites without use of solvent. The composite contains ZnO nanoparticles of 9 nm size that are evenly dispersed on the surface of thermally reduced graphene. The synthesis involves short-time ball milling method using GO and hydrozincite and later they are thermally annealed. At the end, the ball-milled composite was used for the photodegradation of methylene blue under visible light. In one more example, the nanocomposite ZnO@GO (GO decorated with ZnO nanoparticles) was fabricated using solvothermal method, wherein GO and ZnO were prepared using Hummers method and simple thermal oxidation, respectively [55]. The ZnO@GO nanocomposite exhibited improved performance in the photodegradation of methylene blue owing to the vital performance of GO. Herein, GO enhanced the absorption of visible light and lowered the recombination of electron-hole pair. The nanocomposite ZnO@GO demonstrated the highest degradation capacity of 98.5% when irradiated under UV-light for 15 min in neutral solution. However, pure ZnO showed degradation capacity of 49% when irradiated for 60 min. The photodegradation capacity of ZnO nanoparticles was checked for methylene blue dye under sunlight and it showed only 49% efficiency even after 60 min irradiation. In the absence of catalyst, the degradation capacity of methylene blue was 6.5% after 180 min. This shows that the ZnO@GO nanocomposite exhibits improved photocatalytic degradation of methylene blue. It is to be noted that the degradation capacity of the nanocomposite was found to be improved on account of the fine dispersion of ZnO nanoparticles on GO surface. Hence, ZnO@GO nanocomposite exhibits improved photocatalytic performance than that of pure GO and ZnO. In another example, ZnO nanoparticles-rGO nanocomposites were synthesized via sol-gel method with starch as polymerization agent [56]. Herein, long-chain starch compounds played vital role by preventing the growth of ZnO nanoparticles on the surface of rGO and further it contributed in their stabilization. The synthesized ZnO nanoparticles-rGO nanocomposite was used for the photocatalytic degradation of methylene blue and it was observed that the nanocomposite exhibited outstanding improvement in the photocatalytic degradation as compared to that of plain ZnO nanoparticles.

In one example, amine-functionalised graphene nanoplatelets decorated with ZnO nanoparticles were synthesized via hydrothermal method for the photocatalytic degradation of rhodamine B dye [57]. The synthesized nanocomposites exhibited large surface area, higher number

of active sites, improved electron transfer capacity, enhanced light harvesting efficiency and increased separation of photogenerated charge carriers and all these factors contributed for the enhanced photocatalytic degradation capacity of 98.16% under UV light irradiation within 40 min for rhodamine B dye with the remarkable degradation rate of 0.138 min^{-1}. In one more example, rGO/ZnO nanocomposites were synthesized via a novel approach, wherein monodisperse ZnO nanoparticles were deposited on rGO in non-aqueous media using microwave-assisted path [58]. The as-synthesized nanocomposite showed loading of finely dispersed nanocrystals of ZnO on rGO and demonstrated the improved photocatalytic degradation capacity for self-photosensitized dyes like methylene blue and rhodamine B under the irradiation of visible light. From results it can be concluded that loading of ZnO nanocrystals on rGO plays the major role to achieve the finest synergistic effect between ZnO and rGO in the photocatalysis degradation of photosensitized dyes. It was found that rhodamine B dye had well stability under the irradiation of visible light when no catalyst was used but in the presence of rGO/ZnO nanocomposites the photocatalytic degradation of the rhodamine B dye was improved relative to the use of commercial ZnO nanoparticles. The rGO/ZnO nanocomposites exhibited similar results for the photocatalytic degradation of methylene blue dye.

3. CONCLUSION AND FUTURE SCOPE

The outstanding properties such as enlarged surface area and higher number of active sites enable ZnO to adsorb pollutants and facilitates the photogenerated charge carriers to react with pollutants making it an efficient photocatalyst to degrade pollutants. But, absorption of low visible light and photocorrosion has remarkably hindered the photocatalytic performance of ZnO. Several graphene based nanocomposites have been extensively used as a support material to increase the photodegradation capacity of other photocatalysts. To fabricate ZnO/graphene based nanocomposites many tactics were used owing to their structural properties and applications. The prepared nanocomposites exhibited well performance in their photodegradation activity. The coupling of photoactive ZnO and graphene based materials enhanced the photodegradation capacity of ZnO for several dyes. The results showed that proper fabrication of nanomaterials played a vital role in degradation activity. Besides, reusability of ZnO was noticeably enhanced by tailoring the band gap to renovate it into the active photocatalyst under the irradiation of visible light. Graphene improves the properties of the ZnO/graphene based nanocomposites such as it extends the range of light absorption, enhances adsorption and charge separation ability with greater stability.

Now coming to the future scope, it is to be noted that graphene is a carbonaceous substance with outstanding properties that makes it excellent grabbing material. Graphene is conductive in nature and it act as heat sink in different compounds and materials. It has future scope in most of the materials such as glues, paints, varnishes, plastics, inks, foams, induction heaters, concrete, cement and other construction materials, metallurgical processes, catalysts, energy storage materials, pharmaceuticals, biocompatible implants and medical monitoring devices. ZnO is safe, economical and fine UV blocker and can be applied to extend the mechanical properties of synthesized polymer nanocomposites. ZnO based nanocomposites can be successfully used in polymer industry owing to the fabrication of ZnO to reveal UV protection. The electrical, mechanical and optical properties of polymer nanocomposite get enhanced after polymers are added with ZnO nanoparticles due to its large surface area, small size and strong interaction between organic polymer and ZnO nanoparticles. So such nanocomposites may be used in rubber, plastics, coatings and other important applications. The aforementioned properties of ZnO nanoparticles such as electrical conductivity and magnetic properties enable it for extensive applications. ZnO/graphene based nanomaterials can be used in the construction of optoelectronic devices and LEDs. ZnO nanoparticles can even be used in various biological applications such as chemical libraries, tagging etc. and ZnO/graphene nanocomposites may be used for cancer cell detection and DNA detection. ZnO/graphene based nanomaterials can even be used for biosensors development. Wide-range study is needed to use ZnO/ graphene based nanomaterials for their various future applications.

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