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Synthesis and use of bimetals and bimetal oxides in contaminants removal from water: A review

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ABSTRACT

Water pollution aggravates water scarcity by contaminating large volumes of available water. There has been increasing interest in the use of bimetallic particles and bimetallic oxides for the removal of contaminants in water. This paper reviews the recent advances in the development of bimetals and bimetal oxides, and application of them in the treatment of environmental contaminants. 183 published studies (1999–2015) are reviewed in this paper. The synthesis methods of bimetals including chemical methods, physical methods, and biosynthesis methods and the synthesis of bimetal oxides including hydrothermal, impregnation, sol-gel, spray pyrolysis, and precipitation methods were summarized. Then the application of bimetals and bimetal oxides to remove different environmental contaminants in water including chlorinated organic compounds, heavy metal, arsenic and selenium, nitro compounds, and azo dyes, anions and oxyanions were reviewed. The review focuses on experimental conditions, removal efficiency of contaminants, and reaction mechanism in the application of bimetals and bimetal oxides. Compared with monometal, bimetals have

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high catalytic or removal ability for contaminants. The synthesis and application of bimetals and bimetal oxides were remarked.

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1 Introduction

Clean and plentiful water provides the foundation for prosperous communities. We rely on clean water to survive, however, right now we are heading towards a water crisis. The world's thirst for water is becoming one of the most pressing resource issues of the 21st Century. Water pollution adds enormously to the existing problems of water scarcity by contaminating large volumes of available water, which stems from high population growth and growth of cities.

The use of zero-valent metals, such as zinc,[1-3] aluminum,[4-6] and especially iron in contaminants removal has been intensively evaluated in the last five years.[7-10] Although much research has been conducted for contaminates removal by zero-valent iron (ZVI), ZVI processes a greater number of challenges, including the need for high doses,[11] and its long term reactivity being limited due to surface passivation over time.

The limitation of mono metal and metal oxide includes: slow removal efficiency for contaminants,[12-15] easily deactivation,[12,13,16,17] and the removal is easily affected by the pH[17,18]. To improve the reactivity of mono metal and metal oxide, bimetallic particles was developed by coating small amounts of noble metals (Pd, Pt or Ag) or another metal (Ni, Mn or Cu), onto a freshly prepared metal surface. There has been great interest in the use of bimetallic particles for the removal of pollutants in recent years.[19-22] Doping some other metal elements such as Ce, Mn, Ti, Co, and Zr into iron oxides to synthesize bimetal oxides has also become a growing concern for scholars. Bimetal oxides as adsorbents or catalysts to remove a range of contaminants have been studied.[23-26] Bimetals and bimetal oxides play a significant role and have a bright future in contaminants remediation. There is an increasing interest in the use of bimetals and bimetal oxides for the removal of contaminants from water and this is reflected in the overall increasing number of journal articles published in recent ten years (Fig. 1a). Besides, from Fig. 1b, the articles published in the recent ten years occupy 82% of all publications on bimetals and bimetal oxides according to ISI Web of Knowledge data base.

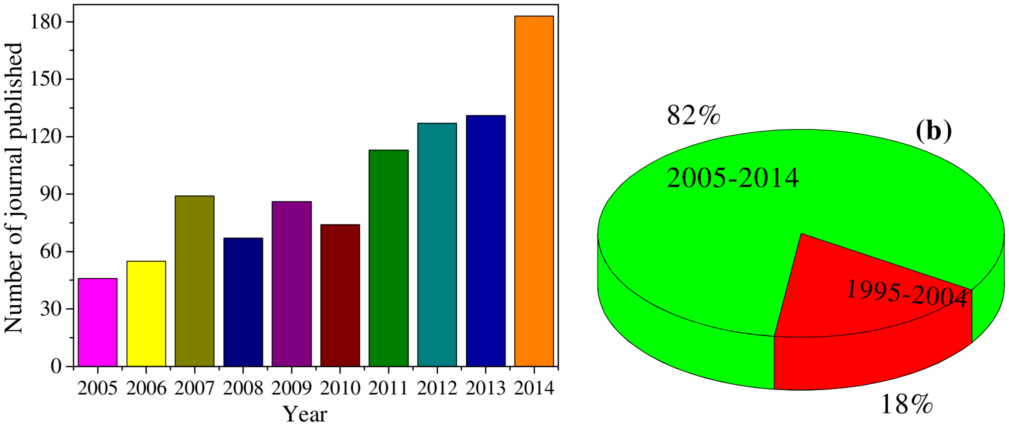

Fig. 1 (a) Number of journal publications on bimetals and bimetal oxides over the past decade, and (b) the percentage of publications on bimetals and bimetal oxides in

1995-2004 and 2005-2014.

At least four review papers on bimetal or bimetal oxides technology have been published in the last five years. They summarized different aspects of science and technology in this field. One review is on the use of ZVI and bimetals of iron in degradation of chlorinated phenols.[27] A work focused on iron oxide nanomaterials in wastewater treatment.[28] O'Carroll reviewed the nZVI/bimetallic nanometals for remediation of sites contamination.[29] The other review was focused on the advance of bimetal Fe nanopartilces in synthesis and application in elimination of environmental pollutants.[30] It can be seen that all the above published reviews were on iron based bimetals or bimetal oxides. To the best of our knowledge, there is no review on the bimetals or bimetal oxides that not only contain Fe, but also does not contain Fe such as Ni/Zn, Cu/Al and their bimetal oxides.

In this paper, the synthesis methods and the use of bimetals and bimetal oxides in the removal of environmental contaminants from water are reviewed. This review focuses on the recent development of synthesis methods of bimetals and bimetal oxides, experimental conditions, removal efficiency of contaminants, and reaction mechanism of bimetals and bimetal oxides with chlorinated organic compounds, heavy metals, arsenic and selenium, nitro compounds and azo dyes, and anions and oxyanions.

2 Synthesis of bimetals and bimetal oxides

2.1 Synthesis of bimetallic particles

Liu et al. summarized the synthesis of bimetallic Fe nanoparticles (NPs),[30] so in this paper we mainly focus on the synthesis methods of bimetals composed of other metals. The synthesis methods of bimetals can be classified into three major types: chemical methods, physical methods, and biosynthesis methods.

2.1.1 Chemical methods

2.1.1.1 Chemical reduction

In this method, metal salts dissolved in a solution are reduced by a reductant. This method is regarded as the most common method for preparing metallic NPs.[31] To synthesize bimetallic particles, two different types of metals are reduced in a solution. Through co-reduction, a kind of chemical reduction, the structure of bimetals can be controlled due to the different redox potential between two metals. The metal with higher reduction potential is reduced first to form a core while the other one is reduced later and precipitates onto the surface of the core metal, which is called core-shell structure.[31,32] Nevertheless, the reduction and the nucleation process are hard to control due to the different redox potential and chemical behaviors of the two metals when stronger reductants were used.[32] There are two approaches to overcome the deficiency. One is to use appropriate surfactants or polymeric ligands to passivate the particle surface and control the reducing procedures. For instance, Cao et al. prepared Au/Pt bimetallic nanochains from their chloride precursors using polyvinylpyrrolidone (PVP) as stabilizer ligand and $NaBH_4$ as the reductant.[33] The other one is to select a weaker reductant. For example, Han et al. synthesized Au/M (M = Pd, Rh, Pt) bimetallic nanocrystals using chloride of Au and M as precursors and oleylamine as reductant.[34] The Au-M bimetallic particles resulted in nanoscale and crystallization. Besides, other mild reductants (such as ascorbic acid and CO) were also used to prepare bimetallic particles.[35,36] Some of other bimetallic materials synthesized by chemical reduction are summarized in Table 1.

Table 1 Bimetallic particles synthesized by chemical reduction

Bimetal	Reducing agents	Metal precursors	Synthesis details	Ref.
Pt/Pd	Ethylene glycol	H_2PtCl_6, Na_2PdCl_4	Reduction of the mixture of Pt/Pd precursors by ethylene glycol in the presence of PVP and $AgNO_3$ at 160 ^{0}C.	37
Cu/Ni	H_2	$Cu(NO_3)_2$, $Ni(NO_3)_2$	Precursors were added in ammonia solution, which was stirred at room temperature for 24 h, ultrasonicated for 3 h, aged for 24 h, and then reduced by H_2 at 773 K for 4 h.	38
Ag/Cu	$NaBH_4$	$AgNO_3$, $CuSO_4$	$NaBH_4$ was slowly dropped to the mixture of two precursors under ice cold condition and nitrogen atmosphere.	39
Au/Ni	$NaBH_4$ and H_2	$HAuCl_4$, $NiCl_2$	A flask containing precursors and sodium dodecyl sulfate was put under ultrasonicator and $NaBH_4$ was added into the mixture. The resulting powers were dried at 50 ^{0}C before they were annealed under a H_2-Ar atmosphere (H_2 vol. 5%) at 750 ^{0}C.	40
Co/Pd	Oleylamine	$PdCl_2$, $Co(NO_3)_2$	Oleylamine was added into a mixture solvent of the precursors at a controlled temperature from 120 ^{0}C to 230 ^{0}C.	41
Pd/Ru	H_2	$PdCl_2$, $RuCl_3$	A mixture solvent of resulting mesoporous silica NPs, ethanol and precursors were reduced by H_2 at 200 ^{0}C for 2 h	42
Au/Pd	$NaBH_4$	$HAuCl_4$, $PdCl_2$	The fresh $NaBH_4$ solution was added into the mixture solvent of precursors and poly vinylalcohol, then the solution was stirred for 30 min to form the NPs.	43
Pd/Ni	H_2	$PdCl_2$, $Ni(NO_3)_2$	Precursors and γ-Al_2O_3 were mixed in acetic	44

	acid solution to form catalyst forerunners. After desiccation, the forerunners powers were reduced by hydrogen (0.15 L/min) in nitrogen at 500 ^{0}C for 2 h.

2.1.1.2 Seeded growth

The method of seeded growth is a commendable approach to prepare core-shell and heterostructure bimetallic compounds.[45] If the surface of seed metal is deposited by the secondary metal, the core-shell structures will form; when the secondary metal deposits on the specific site of the seed, the heterostructure will form. It is significant to adjust the thermodynamic and kinetic parameters during the synthesis of specified morphology of bimetallic particles by seeded growth method.[31] Chen et al. synthesized Cu-based bimetallic nanorods by heterogeneous seeded growth.[45] There are some reports that the structures of bimetallic materials are well-ordered by the seeded growth approach. For example, Adekoya et al. successfully synthesized PVP and dodecanethiol seed mediated Ag/Ru allied bimetallic NPs by seed growth or successive addition method using Ru as seed.[46] The synthesized bimetallic NPs possessed well-ordered core-shell structure. From the recent research of Ko et al.,[47] Au/Ag core-shell NPs with controllable shell thicknesses were generated by seeded growth approach, which can be used to detect adenosine. Han et al. reported that bimetallic Cu-Pt alloy NPs with polyhedral, stellated, or dendritic morphologies were attained by a seeded growth approach.[48] Besides, Yu and He synthesized dendritic Au/Ag bimetallic NPs by the seed-assisted approach,[49] in which Ag was as NPs seed.

2.1.1.3 Diffusion method

Diffusion is an achievable approach to synthesize alloy noble metal nanocrystals with spatially uniform structure (e.g. core-shell structure). Compared with wet chemical reduction methods, diffusion can achieve the aim more easily and mildly.[50] From the research of Zhang et al.,[50] trisoctahedral Au/Pd alloy nanocrystals were formed by diffusion of H_2PdCl_4 and $HAuCl_4$ precursors. They found when the reaction temperature increased to a certain value, the crystal growth rate of an individual component depended only on the rate of diffusion of the precursors to the nuclei surfaces. However, Yu et al. reported that stable Au-AuSn, Au-Sn, AuSn-$AuSn_2$ and $AuSn_2$ nanocrystals were successively formed in the diffusion process at room temperature,[51] which were in intermetallic core-shell structures. With increasing the temperature to 70 ^{0}C, the isolated metallic Sn was generated and cannot diffuse into the precursors of Au nanocrystals.

2.1.2 Physical methods

2.1.2.1 Mechanical alloying method

Mechanical alloying method is a balling milling process in a dry, high energy environment, in which particles are kneaded with each other constantly and re-fractured because of the ball-particle collisions. The particle has the same content as the blended initial particle. The whole procedure of mechanical alloying includes repeated cold welding and fracturing. Bimetallic particles prepared by means of mechanical alloying are widely used for hydrogen generation, dechlorination and hydrogenation.[52-54] Fan et al. prepared a series of Al-based materials via ball milling, which is a widely used mechanical alloying method.[52] Their results showed Bi and Sn can enhance Al reactivity in Al bimetal than Zn, Ca, and Ga. In addition, Al-Bi alloy together with the compounds can accelerate the formation of its mico-galvanic cell between the anode of Al and cathode of Bi.[52] Coutts et al. reported that mechanically alloyed Mg/Pd was prepared by a SPEX 8000M high-energy ball mill with 4-μm-magnesium and palladium impregnated on graphite.[53] Zaranski and Czujko found that the hydrogen desorption kinetics of MgH_2-$FeTiH_x$ composites,[54] which were synthesized by reactive mechanical milling, were affected not only by the phase composition, the milling parameters, and the amount of additive, but also by the milling time.

2.1.2.2 Sonochemical synthesis

Sonochemical synthesis is through the reduction of metal ions by ultrasound waves, which can initiate water homolysis to generate species •H. However, the sonochemical methodology had less been studied compared with other methodologies. Kan et al. reported a composite nano-structure of a core of Au and a shell of Ag with PVP which were prepared under ultrasound using $Ag(NH_3)_2(OH)$ and $HAuCl_4$ as precursors.[55] Anandan et al. reported bimetallic Au-Ag with a core-shell structure was generated sonochemically at 20 kHz in room temperature and Ar atmosphere.[56] Besides, Martínez-Casillas and Solorza-Feria synthesized Pd/Cu bimetals with regular spherical agglomerates using ultrasound, which had an average size of 8 nm.[57]

2.1.2.3 Radiolysis method

Radiolysis is an efficient method to synthesize bimetals.[58] By this method, aqueous solution with metal precursors and stabilizer ligand is irradiated by γ-rays to generate solvated electrons. Metal ions can accept electrons to form metal atoms. Then the metal atoms tend to be aggregated.[32,59] The rate and final nano-structure that the bimetallic particles formed are dependent on the γ-ray dosage. Higher dosages are more likely to form the homogeneous alloys over with core-shell morphologies.[32] This methodology has been widely used to prepare bimetallic particles. For example, Doudna et al. reported that homogeneous crystalline Ag/Pd bimetallic clusters were successfully prepared with Ag_2SO_4 and $PdSO_4$ under γ-radiation which was up to 2 kGy.[59] Moreover, they also reported that bimetallic Ag/Pt NPs were generated with Ag/Pt ions and poly(vinyl alcohol) which was irradiated with gamma rays at dose rates below 0.5 kGy/h.[60] Remita et al. synthesized Au/Pt bimetals with $HAuCl_4$ and K_2PtCl_4 by irradiation with 5 kGy.[61] Mirdamadi-Esfahani et al. used $KAuCl_4$ and H_2PtCl_6 to synthesize Au/Pt bimetallic NPs under high/low dose rate of γ-irradiation.[62]

2.1.3 Biosynthesis method

Biosynthesis method to synthesize bimetallic NPs at room temperature is paid more and more concerns. This method uses non-toxic eco-friendly reductants (e.g. plant extracts, plant powders) to reduce metal ions, which is different from chemical reduction.[63] The functional groups in the reductants play a critical role in reducing and capping the bimetallic particles. This method is frequently applied to synthesize bimetallic NPs. Sheny et al. used the aqueous extract and dried powder of Anacardium occidentale leaf to prepare Au-Ag bimetallic NPs by reducing the precursors of $HAuCl_4$ and $AgNO_3$.[64] They found lower amounts of plant material were sufficient to bring about reduction. Kumari et al. synthesized Au/Ag bimetallic NPs with reducing $HAuCl_4$ and $AgNO_3$ by fruit juice of pomegranate.[65] Phenolic hydroxyls and proteins in the pomegranate fruit extract played an important role in reducing and stabilizing the bimetallic NPs. As shown in Fig. 2, Au/Ag particles were resulted in nanoscale and fcc crystal structure. Mondal et al. reported that the Au/Ag bimetallic NPs were synthesized using aqueous extract of dried leaves of mahogany.[66] Various polyhydroxy limonoids in mahogany leaf extract contributed to reduce and stabilize the bimetallic NPs. The competitive reduction of Au and Ag ions synchronously led to the synthesis of Au-Ag bimetallic NPs, which was similarly reported in the research by Tamuly et al.[67] Apart from Au/Ag bimetallic NPs, Ti/Ni[68] and Au/Pd[63] bimetallic NPs have also been successfully synthesized by bio-reduction method.

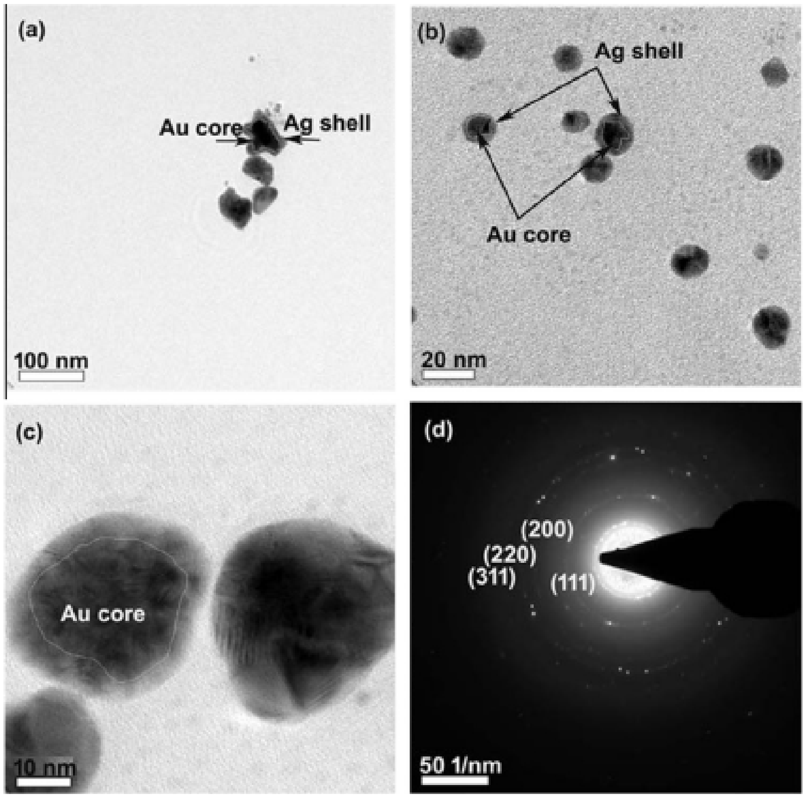

Fig. 2 (a) and (b) TEM images at different magnifications, (c) HRTEM, and (d) SAED pattern of AuAg bimetallic particles with precursor ions respectively in the molar ratio and 1:1 (Adapted with permission from literature 65. Copyright (2015) Elsevier).

2.2 Synthesis of bimetallic oxides

Bimetallic oxides can be synthesized using different methods. The characterization and performance of the bimetallic oxides are both strongly affected by the depositional approaches, the choice and ratio of chemical precursors, components of solvent and temperature of calcination.[69-72] Some representative methods to synthesize bimetallic oxides are hydrothermal method, impregnation method, sol-gel method, spray pyrolysis method, and precipitation method.

2.2.1 Hydrothermal method

Hydrothermal method can prepare bimetallic oxides with porous structures and particular morphologies from metal salts. A facility such as Teflon-lined autoclave is needed to create a condition with spontaneous pressures and special temperature for crystallization of metal precursors.[73] Various bimetallic oxides can be synthesized by controlling the reaction pH, time, temperature, and the composition of reactants in this method. From the research by Somacescu et al.,[74] porous ZnO/Eu_2O_3 bimetallic oxides were synthesized by hydrothermal process using $ZnSO_4$ and $Eu(NO_3)_3$ as precursors and cetyltrimethylammonium bromide as template. Straight strip morphology and hierarchical structure of the oxides were obtained as shown in Fig. 3. Without templates, Su et al. reported Ce/Zr binary oxide NPs with diverse structures, sizes and surface properties through accurate control of the ratio of Ce and Zr were prepared by hydrothermal method.[75] Najafi et al. synthesized the Cu/Mo bimetallic oxides with three-dimensional morphology by hydrothermal method and nanoscale Cu/Mo bimetallic oxides formed by a sonochemical process.[76] They found ultrasonication was unable to influence the crystal structure of the bimetallic oxides. Other bimetallic oxides (e.g. Fe/Mg,[69] Ni/Mo,[77] Co/Mo,[77] Ni/W,[77] Co/W,[77] Fe/Mn,[78] Ti/Zr,[79] and Ni/Mn[80]) have also been synthesized by hydrothermal method.

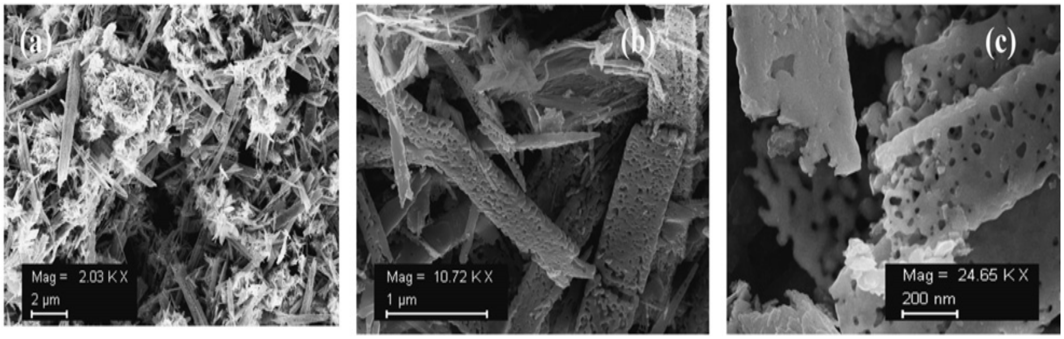

Fig. 3 SEM images (a, b, c) for Zn/Eu_2O_3 (Adapted with permission from literature 74. Copyright (2012) Elsevier).

2.2.2 Impregnation method

This technology is a synthetic process to prepare materials supported bimetallic oxides. In general, one kind of metal oxide or other solid support material prepared previously is impregnated with an aqueous solution of another metal salts or other two metal salts to synthesize bimetallic oxides, and then calcination is carried out. For example, nanosized Zn/Zr binary oxides were synthesized by impregnation method in the research by Ibrahim where the zirconium hydroxide was as a support material.[81] El-Shobaky et al. reported nanostructured Cu and Mn bimetallic oxides and the corresponding monometallic oxides supported on cordierite were obtained through impregnation route.[82] They found the calcination temperature affected the activity of bimetallic oxides supported on cordierite, which was opposite to the single phase supported catalyst. Several bimetallic oxides synthesized by this method are shown in Table 2.

Table 2 Bimetallic oxides prepared using impregnation method

Synthetic	Supported materials	Calcination conditions	Ref.
CuO-MnO/γ-Al_2O_3 MnO-CeO_2/γ-Al_2O_3 CuO-CeO_2/γ-Al_2O_3	γ-Al_2O_3	450 ^0C for 2 h in air	83
TiO_2/ZrO_2	ZrO_2	600 ^0C for 6 h in air	70
MnO_x/CeO_2	CeO_2	550 ^0C for 5 h in air	84
Fe_2O_3/MgO	$Mg(OH)_2$	500 ^0C for 4 h in air	69
Co_3O_4/CeO_2	CeO_2	600 ^0C for 2 h in air	85

2.2.3 Sol-gel method

Sol-gel method is a technology for synthesis of bimetallic oxides with microporous and mesoporous structure. The bimetallic oxide is a result of hydrolyzing and polymerizing the metal precursors with polymerizers to obtain a sol or a gel.[86] Metal alkoxide, metal halide, and metal nitrate are used as the precursors.[70,86,87] Different sol-gel processes, concentrations of templates, and temperatures of calcination can lead to different structures of bimetallic oxides.[71,86,88] As shown in Fig. 4, TiO_2-Al_2O_3 binary oxides with high adsorption capacity and photocatalytic activity was prepared with different surface morphologies by adjusting the concentration of polyethylene glycol and 0.03 mol/L polyethylene glycol was the best concentration.[86] Other researches on the synthesis of bimetallic oxides by sol-gel methods are summarized in Table 3.

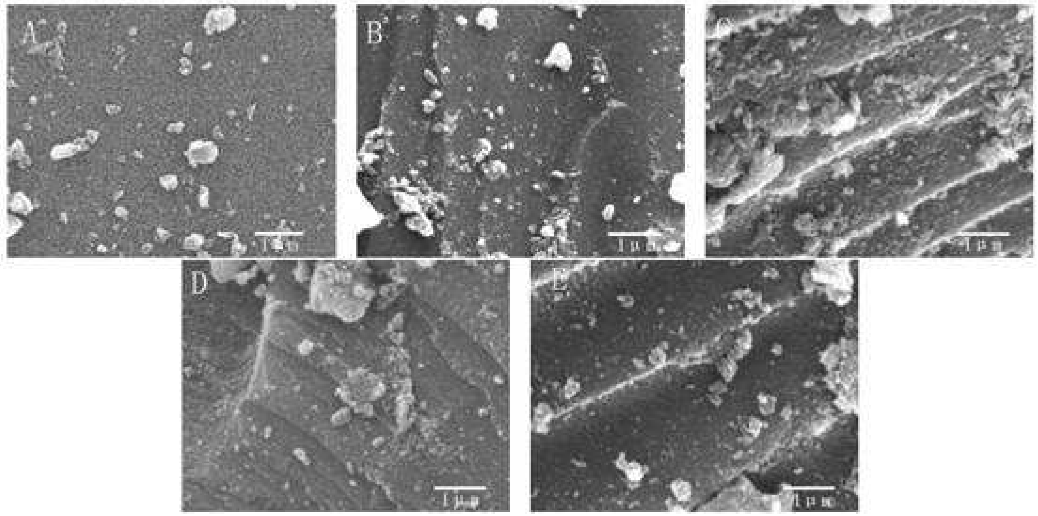

Fig. 4 SEM images of mesoporous TiO_2-Al_2O_3 binary oxides prepared using different concentration of PEG1000: (a) 0 mol/L, (b) 0.012 mol/L, (c) 0.030 mol/L, (d) 0.048 mol/L, and (e) 0.060 mol/L (Adapted with permission from literature 86. Copyright (2012) Hindawi).

Table 3 Synthesis of bimetal oxides by sol-gel methods

Synthetic	Precursor	Solvent	Gelata	Calcination conditions	Ref.
Al_2O_3/La_2O_3	Al(O-Sec-But.)$_3$, La(acac)$_3$	Ethanol	2-methyl-2,4-pentanediol	650 ^{0}C for 4 h in air	89
$Ca_2Fe_2O_5$	$CaCl_2$ from shells of African land snail, $FeCl_3$	H_2O	NaOH	1100 ^{0}C in air	90
Fe/Co oxide	$Co(NO_3)_2$, $Fe(NO_3)_3$	H_2O	Citric acid	800 ^{0}C for 2 h in air	91
Ca/actinide (Th and U) oxide	Calcium nitrate, actinide nitrate	Ethylene glycol	Citric acid	900 ^{0}C for 5 h in air	92
CaO/Al_2O_3	AlOOH prepared from $Al(OBu)_3$, $Ca(NO_3)_2$	Ethanol	NA	1100 ^{0}C for 3 h in air	93
TiO_2/ZrO_2	$Ti(OCH(CH_3)_2)_4$, $Zr(OCH_2CH_2CH_3)_4$	Ethanol and water	NA	550 ^{0}C for 2 h in air	94

NA: not available

2.2.4 Spray pyrolysis method

In spray pyrolysis method, bimetal oxides thin films and nano-powders can be effectively and easily prepared in an equipment. For preparation of bimetallic thin films, bimetallic precursors were sprayed and deposited on substrates in an apparatus with regular parameters (e.g. temperature, solution flow rate, nozzle to substrate distance and carrier gas pressure), which can affect the structure and grain size of the film.[95,96] For preparation of nano-powders, the viscous gel of bimetallic precursors are firstly obtained, then the gel undergoes a smouldering burning in a device such as a furnace with a relatively higher temperature where plenty of ashes can generate. The product ashes are crushed to obtain powders.[97,98] However, the characteristics of the powders varied with the temperature of calcination following the ashes crushing. Zhang et al. reported a mild, ultrafast and eco-friendly spray pyrolysis strategy to prepare nano-phase $ZnMn_2O_4$.[99] In their research, precursory solution of manganous and zinc acetate were sprayed into a tubular furnace with a high speed of 1 mL/s while precursory solution of these two acetate with absolute ethanol and ethylene glycol relatively were treated under the same conditions. Interestingly, these three kinds of resultants revealed the same phase and structure of $ZnMn_2O_4$ NPs and ethylene glycol can increase the specific surface area and pore volume of the particles.

2.2.5 Precipitation method

Precipitation including co-precipitation and asynchronous precipitation is a simple and popular wet chemical method for synthesis amorphous nano-structure bimetallic oxides.[100,101] Precursors of metal salts are precipitated by adjusting the pH value to alkalescence or alkalinity with precipitants such as sodium hydroxide and ammonia. Moreover, calcination with appropriate temperature followed by the separation of the sediments is needed to generate particles with small size and high specific surface area, whereas improper temperature can lead to the decrease of specific surface area.[102,103] However, the disadvantage of agglomeration can appear during the process of preparation. The addition of dispersing agents and stabilizers can be an effective method.[72,104,105] Other studies on synthesis of bimetallic oxides by precipitation method are summarized in Table 4.

Table 4 Synthesis of bimetallic oxides by precipitation method

Bimetal oxides	Precursor	BET surface area (m^2/g)	Precipitant	Temperature (^0C)	Calcination conditions	Ref.
Fe/Mn	$KMnO_4$, $FeSO_4$	231	NaOH	25	NA	106
Fe/Zr	$FeCl_2$, $ZrOCl_2$	106.2	NaOH	50	500 ^0C in air for 4 h.	107
Fe/Mn	$FeSO_4$, $MnCl_2$	above 200	Oxalic acid	0	300 ^0C in air for 1 h with heating rate of 1 ^0C /min.	108
Zr/Mn	$Zr(NO_3)_4$, $Mn(NO_3)_2$	127.4-144.5	Ammonia	Room temperature	500 ^0C for 5 h in air.	109
Fe/Zr	$FeCl_3$, $ZrOCl_2$	74.61	NaOH	60	NA	110
Zr/Mn	Mn(VII) salt, Mn(II) salt, Zirconium salt	213	NA	Room temperature	NA	111
Fe/Mn	$FeCl_3$, $FeSO_4$,	NA	NaOH	Room temperature	NA	112

	$MnSO_4$					
Ce/Mn	$Ce(NO_3)_3$, $Mn(NO_3)_2$	106	Na_2CO_3	Room temperature	550 ^{0}C for 6 h in air.	73
Ti/Al	$TiCl_4$, $AlCl_3$	186-218	Ammonia gas	Room temperature	500 ^{0}C for 6 h in air.	113
Sn/Mn	$SnCl_4$, $Mn(NO_3)_2$	47.9-54.0	Aqueous ammonia	Room temperature	500 ^{0}C for 5 h in air.	114
Cr/Zr	$Cr(NO_3)_3$, $ZrOCl_2$	59.9-220.8	Aqueous ammonium	60	500 ^{0}C for 3 h in air.	115
Mg/Al	$Mg(NO_3)_2$, $Al(NO_3)_3$	52.1-83.4	NaOH	Room temperature	At 600, 800 and 1000 ^{0}C, respectively, for 3 h in air.	116

NA: not available

3 Application of bimetals and bimetal oxides for the removal of contaminants

3.1 Removal of chlorinated organic compounds (COCs)

3.1.1 COCs removed by bimetals

COCs are ubiquitous contaminants in environment, which pose a great threat to human health, since they are recalcitrant, lipophilic, and can be bioaccumulated through food chain.[117] In recent years, bimetal-catalyzed dechlorination has become one of the hotspots in the chemical degradation of chlorinated toxic organic compounds (Table 5). Just take the most typical Fe based bimetallic system for example, in bimetallic system, a second metal M (such as Pd, Ni, Pt, and Cu) deposited on metal substrate serves as a promising alternative hydrodechlorination reagent and the active hydrogen species produced from the corrosion of metal substrate is further stored in M lattice. Besides the catalytic function, the galvanic effect between the Fe anode and the stable M cathode can also improve the reactivity due to the increase of corrosion of metal substrate.

Table 5 Selective of catalytic removal of COCs by different bimetallic particles

COCs	Bimetal	Optimum pH	Dosage and ratio of bimetal	Removal efficiency	Ref.
2-chlorobiphenyl	Pd/Al	3.0	5.0 g/L, 1.43 wt.% Pd	100%	118
Hexachlorobenzene	Cu/Fe NPs	≤4.0	NA, 5.0 wt.% Cu	98%	119
2,4-dichlorophenol	Pd/Fe NPs	5.7	6.0 g/L, 0.20 wt.% Pd	99.4%	120
Dichlorodiphenyltrichloroethane	Ni/Fe NPs	4~10	0.05 g/L, Ni/Fe molar ratio is 1:3.5	>90%	121
1-(2-chlorophenyl) ethanol	Pd/Fe	5.59	20.0 g/L, 0.10 wt.% Pd	100%	122
2,4,6-trichlorophenol	Pd/Zn, Ni/Zn, Cu/Zn, Pt/Zn	4.9	200.0 g/L, Pd, Ni, Cu and Pt content is 636, 1269, 1272, and 887 ppm (mg of catalytic metal/kg of base metal)	100% was only observed in Pd/Zn	123
Hexachlorobenzene	Pb/Fe	7.0	84.2 g/L, 1.4 wt.% Pb	99%	124
3-chlorophenol	Pd/Al NPs	3.0~4.0	2.0 g/L, 1.16 wt.% Pd	99.7%	125
Pentachlorophenol	Ni/Fe NPs	5.3	12.0 g/L, 0.5 wt.% Ni	100%	126
γ-Hexachlorocyclohexane	Pd/Fe NPs	6.5	0.5 g/L, total iron content 59.2%	100%	127
Dichloromethane	Cu/Al	10.0	60.0 g/L, 20 wt.% Cu	98%	12
Tetrachlorobisphenol A	Pd/Fe	6.0	6.0 g/L, 0.044 wt.% Pd	100%	13
1,2,3,4-TCDD	Ag/Fe	6.85	20.0 g/L, 0.006 mol% Ag	>90%	14

Carbon tetrachloride	Fe/Al	6.7	10.0 g/L, Fe/Al molar ratio is about 2:3	100%	16

NA: not available

The use of Fe based bimetals in removing COCs achieved great success, but its reactivity may be hard to remain in an extended run due to the spontaneous and uncontrollable ZVI corrosion. The corrosion causes the loss of catalyst base, iron oxide precipitation, and excessive H_2 formation, which further leads to the deactivation of M/Fe.[128] As to the bimetallic NPs, the reactivity is greatly improved because the decrease in particle size can lead to a higher intrinsic reactivity and less mass transfer restrictions. However, due to the very high reactivity, the deactivation of bimetallic NPs is quite easy and rapid through the formation of metal oxide encapsulation or agglomeration. It is reported that the loading NPs onto carbon microspheres or polymeric granules and adsorption of the polymer or surfactant on the surface of bimetallic NPs can hinder the agglomeration.[129] Nevertheless, these modification methods of bimetallic NPs will obviously increase the cost-efficiency in their further application. Furthermore, the removal mechanism of the hydrodechlorination by bimetals varied at different pH values. The electron transfer is through the formation of the galvanic cells at higher pH, whereas at low pH mainly via direct reduction of H^+.[130]

New attempts were made with the introduction of other active metal to replace Fe as the substrate in bimetallic systems, such as Sn,[17] Zn,[123] Mg,[131] and Al[132]. Agarwal et al. prepared Pd/Mg bimetals through a simple wet-chemistry procedure,[133] in which Pd^0 was reductively deposited onto Mg by intimately mixing it with a palladium nanoparticle precursor in ethanol. The synthesized Pd/Mg bimetals were used to dechlorinate 2-chlorobiphenyl, and the performance for 2-chlorobiphenyl dechlorination in the presence of naturally abundant anions was evaluated. Inspired by the study of Agarwal et al., Yang et al. selected Mg, Al, Mn, Zn, Fe, Sn, and Cu as the substrates of the Pd-loaded bimetallic particles.[118] They investigated the catalytic hydrodechlorination of 2-chlorobiphenyl in aqueous solution with these Pd-loaded bimetallic particles and found that Pd/Al particles had the highest stability and relatively high reactivity in acid aqueous solution (Fig. 5). Pd/Mg and Pd/Al particles exhibited to be effective for hydrodechlorination mainly because Mg and Al possess significantly lower standard electrode potential and unique corrosion properties, resulting in a greater force to drive the hydrodechlorination reaction.

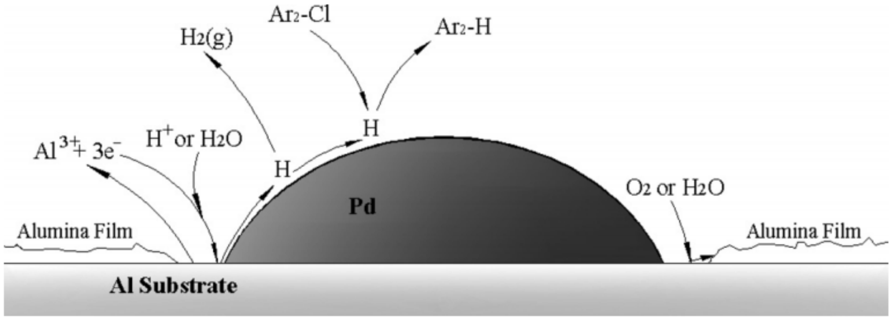

Fig. 5 Proposed mechanism for the hydrodechlorination of 2-chlorobiphenyl on Pd/Al bimetallic particle in acidic solution (Adapted with permission from literature 118. Copyright (2011) Elsevier).

3.1.2 COCs removed by bimetal oxides

Compared with mono-metallic oxides, bimetal oxides have two advantages. First, the change of physical properties like surface area, surface charge, porosity, and crystallinity might enhance the catalytic activity and adsorption capacity;[15] Second, bimetal oxides combined the advantages of different oxides.[134] Using bimetallic composite oxides as the catalysts for hydrodechlorination had achieved great success just as the bimetals. Zhou et al. studied the catalytic Al/Mg composite oxide on the degradation and dechlorination of PVC-containing mixed plastics.[135] The comparative experiments in Al/Mg composite oxide, MgO, and γ-Al_2O_3 revealed that Al/Mg composite oxide had a good combination of the advantages of MgO and γ-Al_2O_3. Therefore, the Al/Mg composite oxide catalyst showed both cracking and dechlorination ability can be effectively used for catalytic degradation and dechlorination of PVC-containing mixed plastics. Ma et al. investigated the dechlorination of hexachlorobenzene with a mixture of commercial CaO and α-Fe_2O_3 (CaO/α-Fe_2O_3) in closed systems at temperatures of 300 ^{0}C and 350 ^{0}C.[136] They found that the dechlorination efficiency was dramatically enhanced due to the remarkable synergic effect of CaO/α-Fe_2O_3 compared with CaO or α-Fe_2O_3 alone. The proposed mechanism showed that unsaturated iron ions at the surface serve as an initial adsorption sites for hexachlorobenzene leading to the breakage of C–Cl bond, and calcium servers as a sink for chlorine ion regenerating iron oxide.

3.2 Removal of heavy metals

3.2.1 Heavy metal removed by bimetals

Owing to the toxicity effects of heavy metal on human and wildlife, non-biodegradable, and bioaccumulation even at relatively low concentration, heavy metal contamination has gained great concerns.[137] The toxicity of heavy metals in the environment depends on its transformation, solubility, and mobility, which are governed by redox reactions, precipitation/dissolution reactions, and adsorption/desorption phenomena.[29] Consequently, these mechanisms are often involved in water treatment strategies for removing heavy-metal pollutants.[138]

Recent advances have shown that bimetals with great redox activity and adsorption capacity can effectively remove heavy metals ions. The most typical bimetals proposed in the remediation of heavy metal contamination is bimetallic Fe or bimetallic Fe NPs. With the introduction of a second metal like Pd, Ag, Ni, Pt, and Zr with ZVI or ZVI NPs, the formed bimetallic system can provide more surface active sites and increase heavy metal removal efficiency. Their galvanic cells effort can also accelerate the heavy metal removal efficiency. The use of bimetallic Fe or bimetallic Fe NPs for reductive removal of heavy metal such as Cr(IV), Cd(II), and Cu(II) achieved great success.[139-141] Moreover, stabilizing bimetallic Fe NPs in a matrix which has certain properties of absorption of inorganic contaminants can ameliorate its capability of eliminating heavy metal contaminants. For example, Kadu et al. investigated the remediation of Cr(VI) by Fe–Ni bimetallic NPs and their nanocomposites prepared with montmorillonite (MMT) clay (Fig. 6),[142] which included in situ formed and loaded Fe–Ni NPs on MMT. The incorporation of Fe/Ni NPs into MMT clay matrix guaranteed the proper dispersion of NPs and the removal capacity was enhanced mainly due to the adsorption tendency of MMT as well as reduction capacity of NPs. The recycle experiments demonstrated that only the in suit formed Fe/Ni NPs on MMT kept 100% removal in the first 3 cycles.

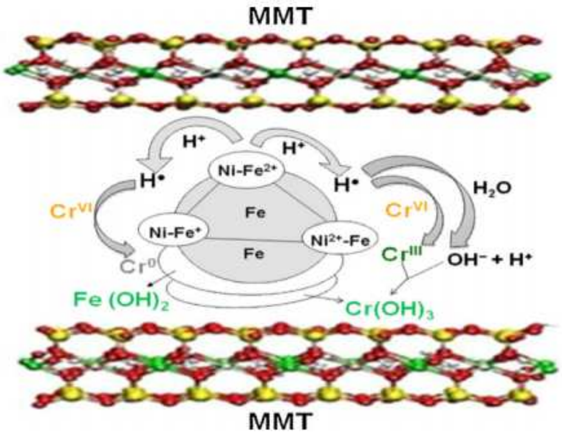

Fig. 6 Schematic diagram of mechanism pathway for Cr(VI) reduction by Fe/Ni NPs (Adapted with permission from literature 142. Copyright (2011) Elsevier).

3.2.2 Heavy metal removed by bimetal oxides

Just like bimetals, bimetal oxides also demonstrated a remarkable capacity in elimination of heavy metal contamination. The bimetal oxides were employed to remove heavy metal ions such as Sb(III),[106] Cr(VI),[143] and Co(II) [144]. Different from the bimetals, bimetal oxides normally used as adsorbents in the removal the heavy metal ions. Therefore, the removal mechanism of heavy metals by bimetals and bimetal oxides are not the same (Table 6).

Table 6 Mechanisms of the heavy metal removed by bimetals and bimetal oxides

Heavy metal	Bimetals or bimetal oxides	Optimum pH	Removal capacity (mg/g)	Mechanism	Ref.
Cr(VI)	Ag/Fe NPs	2.0	55.18	Reduction	145
Cd(II)	Au doped nZVI particles	9.0	188	Reduction and adsorption	146
Pb(II)	Fe/Mg (hydr)oxides	5.0 ~10.0	95.88	Adsorption	147

Cu(II)	Co/Fe_2O_3 NPs	6.0	50.9	Adsorption	148
Sb(V)	Fe/Zr oxide	≤5.5	51	Adsorption	134

Hu et al. reported an ingenious strategy for the recycling of Cr(VI)-enriched sorbents,[149] which are Zn/Al-based nanocomposites with a Zn to Al ratio of 4:1. These Zn/Al-based nanocomposites not only behave as a sorbent, but a photocatalytic function can be evolved by calcination. The Zn/Al composite sorbents showed good removal capacities for Cr(VI) even after repeated absorption cycles. Liu et al. investigated the simultaneous removal of Cd(II) and Sb(V) by Fe/Mn binary oxides.[150] They found that the simultaneous adsorption of Sb(V) and Cd(II) onto Fe/Mn binary oxides can be achieved over a wide initial pH range from 2 to 9, and the Cd^{2+} showed higher affinity towards Fe/Mn binary oxides than Ca^{2+} and Mn^{2+}.

3.3 Removal of arsenic and selenium

Arsenic (As) and selenium (Se) are not heavy metal elements, but they show similar toxicity of heavy metals, consequently they are classified as semi-metallic elements. The most typical method for the removal of As and Se is adsorption. Bimetal oxides are reported to be excellent adsorbents for the removal of As and Se.[26,105,151-155]

Basu et al. summarized that among the adsorbent materials investigated for arsenic removal, the performances of the mixed metal oxides were found to be superior to that of the individual oxides.[156] Zhang et al. prepared a novel Fe–Mn binary oxide by low cost materials using a simultaneous oxidation and coprecipitation method.[157] The Fe–Mn binary oxide can not only completely oxidize arsenite (As(III)) to arsenate As(V), but also can effectively remove both As(V) and As(III), particularly the As(III), attributing to the combination of the oxidation property of manganese dioxide and the high adsorption features to As(V) by iron oxides. In their further study, they employed X-ray absorption spectroscopy to investigate the change of the oxidation state of arsenic and manganese during As(III) sorption (using X-ray absorption near-edge structure) and to determine the mechanisms of arsenic sorption in single and binary systems of Fe and Mn oxides (using near-edge X-ray absorption fine structure).[158] The results showed that the MnO_x content is mainly responsible for oxidation and the FeOOH content is dominant for adsorption, and the As surface complex is an inner-sphere bidentate binuclear corner-sharing complex (Fig. 7). Zhang et al. synthesized bimetal oxide magnetic nanomaterials ($MnFe_2O_4$ and $CoFe_2O_4$) and employed them to remove As(III) and As(V).[159] The maximum adsorption capacities of As(III) and As(V) on $MnFe_2O_4$ were 94 and 90 mg/g, and on $CoFe_2O_4$ were 100 and 74 mg/g, respectively. $MnFe_2O_4$ and $CoFe_2O_4$ showed higher As(III) and As(V) adsorption capacities than the referenced Fe_3O_4, which might be caused by the increase of the surface hydroxyl (M–OH) species.

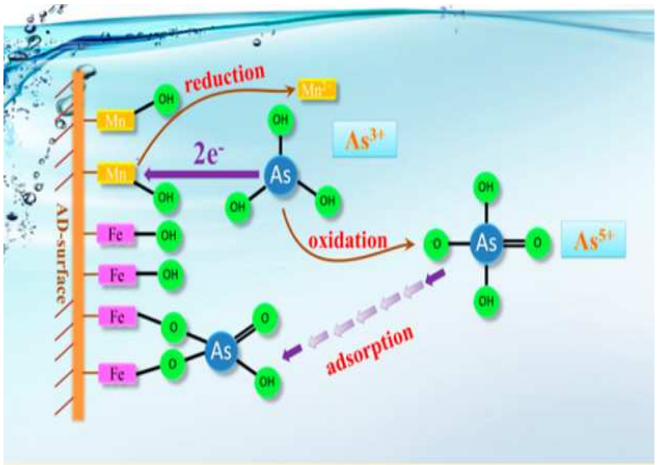

Fig. 7 Schematic diagram of mechanism pathway for As(III) removal by Fe–Mn binary oxide (Adapted with permission from literature 158. Copyright (2014)

American Chemical Society).

Sun et al. investigated the removal of Se(IV) and Se(VI) by three types of MFe_2O_4 (M = Mn, Cu, Co) spinel ferrite NPs,[160] which were prepared through a hydrothermal method. Due to their simple synthesis process, high saturation magnetization, and excellent performance, $CuFe_2O_4$ and $CoFe_2O_4$ can be promising adsorbents for Se(IV) and Se(VI) removal compared with $MnFe_2O_4$.

3.4 Removal of nitro compounds and azo dyes

3.4.1 Nitro compounds and azo dyes removed by bimetals

Nitro compounds are usually classified into nitro aliphatic and nitro aromatic compounds. Compared with nitro aliphatic compounds, nitro aromatic compounds have a broader application and harder to be degraded, leading a more widely detection in the environment. Azo compounds are another widespread nitrogenous compounds in the environment, especially azo dyes, which contain one or more azo (N=N) bonds, are the most important and largest class of synthetic dyes used in commercial applications.[161] Due to the existence of N–O and N=N bonds, nitro or azo compounds are refractory pollutants in the environment.

The use of bimetals or bimetallic NPs in the elimination of nitro compounds are well reported, especially in the degradation of some persistent nitro aromatic compounds (Table 7). Xiong et al. executed a comparative study on the reactivity of Fe/Cu bimetallic particles and ZVI in the degradation of p-nitrophenol under different aeration conditions.[167] Results showed that dissolved oxygen can improve the mineralization of p-nitrophenol, and Cu can enhance the reactivity of ZVI.

p-nitrophenol was degraded into nontoxic and biodegradable intermediate products, and subsequently mineralized into CO_2 and H_2O. Kim et al. investigated the reduction of nitro compounds and olefins by Pd/Pt bimetallic NPs on functionalized multi-wall-carbon nanotubes.[168] They found Pd/Pt bimetallic NPs on functionalized multi-wall-carbon nanotubes have remarkable activity for efficient chemoselective reduction of nitro compounds without any loss of activity in the 10 times recycles.

Table 7 Nitro compounds and azo dyes removal using bimetals and bimetallic NPs.

Nitro compounds or azo dye	Bimetals or bimetal NPs	Optimum conditions	Removal efficiency	Ref.
Hexahydro-1,3,5-trinitro -1,3,5-triazine	Bi/Fe NPs	1.0 g/L Bi/Fe, 4%-Bi/Fe^0 (atomic ratio) at pH 3.0	100%	162
Hexahydro-1,3,5-trinitro -1,3,5-triazine, High Melt Explosive, trinitrotoluene, Nitrotriazolone, Nitroguanidine, 2,4-dinitroanisole	Fe/Cu	3% solid/liquid (S/L) Fe/Cu loading 9.7 wt.% Cu at pH 3.0	100%	163
Para-nitrochlorobenzene	Pd/Fe	40 g/L Pd/Fe, 0.03 wt.% Pd at pH 6.5	100%	164
2-, 4-nitrophenols	Fe@Au NPs	1.4 g/L Fe@Au, 0.06 M $NaBH_4$ at pH 7.2	100%	165
Acid black 1	Cu/Fe	0.5 g/L Cu/Fe, Cu/Fe ratio (wt) 1:1 at pH 9.0	94% TOC removal	166
Methylene blue	Cu/Fe	100.0 g/L Cu/Fe, Cu/Fe ratio (wt) 1:4 at pH 6.0-9.0	98% color removal	18

The performances of bimetals or bimetallic NPs in the catalytic reduction of azo dyes have been investigated thoroughly in recent years, since they are considered as effective catalysts to break the N=N bonds in the azo dyes. Bokare et al. reported the reductive degradation of azo dye Orange G in aqueous solution using the Fe-Ni bimetallic NPs.[169] They found that the reductive cleavage of the azo linkage leads to the formation of aniline and naphthol amine derivatives with the latter remaining adsorbed on the particle surface.

The leaching of toxic heavy metal from bimetals will lead to great threats to our life and environment. Therefore, various versatile catalyst supports were utilized to suppress metal leaching, which may bring excellent catalyst performance and practicability. Cai et al. prepared two supported bimetallic catalysts of Fe-Co/GAC and Fe–Co/SBA-15 and employed them in the ultrasound enhanced heterogeneous activation of peroxydisulfate and peroxymonosulfate process to degrade Acid Orange 7 and Orange II, respectively.[170,171] The sulfate radicals ($SO_4^{-\bullet}$) were assumed to be the dominating reactive species for the Orange II decolorization in the US/Fe–Co/SBA-15/PMS system (Fig. 8). Both Fe-Co/GAC and Fe–Co/SBA-15 exhibited good activity and stability in the decolorization of Acid Orange 7 and Orange II.

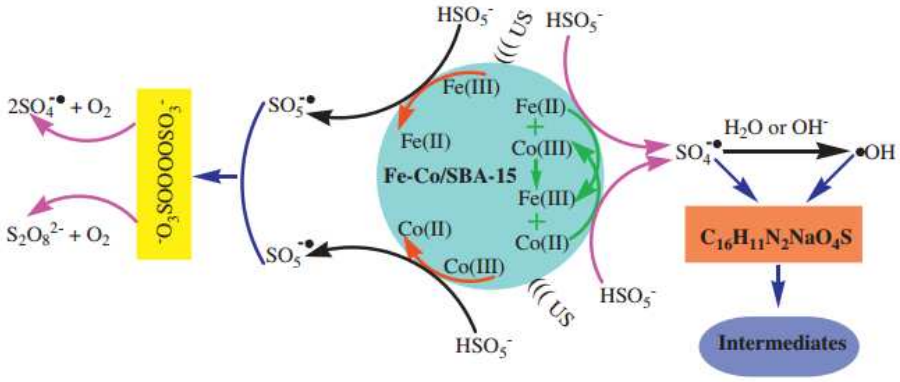

Fig. 8 Proposed mechanism of US/Fe-Co/SBA-15/PMS system (Adapted with permission from literature 171. Copyright (2015) Elsevier).

3.4.2 Nitro compounds and azo dye removed by bimetal oxides

Bimetal oxides are also well reported in the removal of nitro compounds and azo dyes. Hua et al. investigated the degradation process of two dyes through catalytic wet air oxidation with the catalysts CuO/γ-Al_2O_3 prepared by consecutive impregnation.[172] Results indicated that the degradation of dyes began with the cleavage the azo bond, proceeding with the oxidation of the lower molecular weight intermediate, and resulting in the complete mineralization of dye to CO_2 and H_2O. The CuO/γ-Al_2O_3 catalysts exhibited a remarkable reactivity with CuO acting as O_2 transfer carrier and the high surface area, low cost, and high strength γ-Al_2O_3 acting as carrier.

Besides γ-Al_2O_3, some efforts have been made on the use of iron oxide NPs as support to develop the magnetically recoverable nanocatalysts for the removal of nitro compounds and azo dyes. Chiou et al. have successfully synthesized Ag/Fe oxide composite NPs via a facile one-pot green process.[173] The use of Ag/Fe oxide composite NPs for 4-nitrophenol removal revealed its high activity and stability, giving this magnetically recoverable nanocatalysts a promising future in wastewater treatment. Safavi et al. investigated the degradation of the selected azo dyes using a novel palladium/hydroxyapatite/Fe_3O_4 nanocatalyst.[174] The high catalytic activity, magnetic separatability and good stability of palladium/hydroxyapatite/Fe_3O_4 nanocatalyst make it a good alternative for decontamination.

3.5 Removal of anions and oxyanions

3.5.1 Anions and oxyanions removed by bimetals

The anions and oxyanions in aqueous system coming from the natural and anthropogenic processes pose a great threat to human and other living creature. For example, some anions and oxyanions of the halogen elements are of particular concern due to their toxicity, mutagenicity, carcinogenicity, and radioactivity.[175] Besides halogen anions and oxyanions, nitrate, sulfate and phosphate are all widespread anion constituents in surface water, groundwater, and wastewater. Membrane techniques,[176] adsorption,[177] and selective reduction are all alternative strategies for the elimination of these anions and oxyanions.[178]

It is well recognized that the ideal way to removal nitrate is via the selective reduction of NO_3^- to N_2 without further reduction to NH_4^+ or NH_3. Bimetals have been proposed to use in the selective reduction of nitrate and achieved success. Liou et al. investigated the selective reduction of NO_3^- to N_2 using bimetallic particles of Pd/Zn, Pt/Zn, and Cu/Zn at neutral pH.[179] They found that compared with the naked iron and zinc, the selectivity of N_2 production is highly promoted after the bimetals deposition.

Different from the reduction of NO_3^- and NO_2^-, the final products are often halogen anions (Cl^- and Br^-) in the reduction of halogen oxyanions, because of the high reactivity of the intermediate products (such as ClO^- and Cl_2). Bimetals are good candidates for the catalytic reduction of halogen oxyanions. Choe et al. has proposed that a Re/Pd bimetal catalyst may be useful for the treatment of perchlorate-contaminated water, especially as part of a hybrid ion exchange/catalytic reduction process.[180] They investigated the influence of rhenium speciation on the stability and activity of Re/Pd bimetals for the catalytic reduction of perchlorate.[180] Re sorption under different redox conditions result in the different Re speciation on the catalyst outer surface. As for practical applications, it is strongly recommended that Re/Pd with lower Re contents and avoid longer-term exposure to oxic waters for the sake of stronger interactions, greater stability and longer catalyst lifetimes. Based on this conclusion, Liu et al. further studied the application of a Re-Pd bimetallic catalyst for treatment of perchlorate in waste ion-exchange regenerant brine.[181] Results showed that the co-contamination of the ion-exchange waste brine by excess NO_3^- was the major cause of the deactivation of the Re-Pd catalyst. As a pre-treatment of NO_3^-, a separate bimetallic catalyst (In-Pd/Al_2O_3) was used to improve the selectivity for N_2 over NH_4^+ and enabled facile ClO_4^- reduction by the Re-Pd catalyst, with which making this sequential catalytic treatment a promising strategy for enabling reuse of waste ion-exchange brine containing NO_3^- and ClO_4^- (Fig. 9).

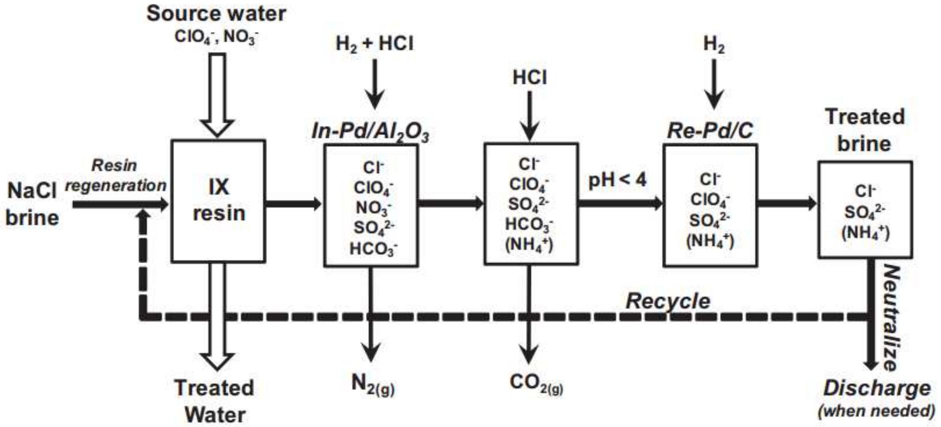

Fig. 9 Sequential catalytic treatment strategy for recycling waste ion-exchange regenerant brines contaminated by ClO_4^- and NO_3^- (Adapted with permission from literature 181. Copyright (2013) Elsevier).

3.5.2 Anions and oxyanions removed by bimetal oxides

Compared with the bimetal, bimetal oxides usually serve as a sorbents in the removal of anions and oxyanions. Moriyama et al. used the Mg–Al bimetal oxides as a sorbents for the removal of F^- in aqueous solutions.[116] They found that a higher calcinations temperature will result in the formation of the additional $MgAl_2O_4$ phase, which did not contribute to the immobilization of F^-. Thakre et al. investigated the performance of the chitosan based mesoporous Ti/Al binary metal oxide supported beads for fluoride removal from drinking water.[182] The excellent defluoridation capacity with negligible release of aluminium and titanium ions and the highly reusability of the adsorbent shows its promising application in practice.

As phosphate is a necessary nutrient for the growth of most organisms, the removal of phosphate from water is of great importance to control eutrophication. Lu et al. examined the performance of a nano-structured Fe/Ti bimetal oxide sorbent in the removal of phosphate from aqueous solution.[183] They found that the Fe/Ti bimetal oxide prepared with a Fe/Ti molar ratio of 20:1 was the optimal sorbent and its Langmuir sorption capacity for phosphate was 35.4 mg/g at pH 6.8, which excel most of reported Fe oxide-based sorbents. The main mechanism of phosphate absorption was the replacement of surface hydroxyl groups by phosphate via formation of innersphere surface complex.

4 Remarks and conclusions

There has been great interest in the use of bimetals and bimetal oxides for the removal of environmental contaminants and encouraging treatment efficiencies have been documented. This paper gives an overview of the recent advances of the synthesis methods and application of bimetals and bimetal oxides.

Catalytic properties of bimetals and bimetal oxides depend on their structure, size, shape, composition, and surface property, all which are affected by different preparation procedures. Among the synthesis methods of bimetals, chemical methods are more widely used, however, they often occur in presence of toxic solvents and reducing agents. Physical methods are green and environmentally friendly, however, they often require complicated equipments. Biosynthesis method using non-toxic and eco-friendly reductants is frequently applied to synthesize bimetallic NPs. Among all the methods to synthesize bimetal oxides, precipitation method is a popular and widely used method. The addition of dispersing agents and stabilizers can overcome the disadvantages of agglomeration during the preparation. Hydrothermal method can prepare bimetallic oxides with porous structures and particular morphologies from metal salts. Sol-gel method is a low cost and simple method to prepare bimetal oxides with excellent compositional control, high homogeneity at the molecular level, and low crystallisation temperature.[88] However, sol-gel method needs calcination, which is similar to impregnation method. Spray pyrolysis method can prepare bimetal oxides effectively and easily, however, it needs a high reaction temperature and an equipment to spray precursors. Precipitation method is beneficial to prepare amorphous bimetallic oxides and the specific surface area of the oxides is affected by the calcination temperature.

To sum up, current preparation methods for bimetals and bimetal oxides are often complex and high cost. So the future research may decrease the cost by finding new low-cost raw materials, and develop more simple and practicable methods.

The application of bimetal or bimetal oxides in the removal of contaminants have achieved great success, however, the roles of bimetals or bimetal oxides played in the removal of these contaminants are not the same. In bimetals, a substrate metal combines with a second metal M, which serves as a promising alternative hydrodechlorination and hydrogenation reagent and a storage of the active hydrogen species. Its remarkable catalytic function turns bimetals into good catalysts for the hydrodechlorination of COCs, nitroaromatic compounds, and azo dyes. Considering the high reducibility of bimetals, they are also employed as reductants for the removal of Cr(VI) and some oxyanions. In the bimetal oxides, the metal oxide with low reactivity and low cost are used as host metal oxides, while the other metal oxide with high reactivity acts as functional metal oxides. Bimetal oxides with the combination of advantages of two oxides not only can be good sorbents, but also can be good reductants/oxidants or catalysts in the removal of contaminants.

The leaching of metal ions from bimetals or bimetal oxides raises concern on the decreased catalyst longevity, high costs, and potential secondary metal contamination to the treated wastewater. So explore methods to decrease the metal leaching is another future research.

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